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Syntheses and X-ray investigations within the system FeS_2-CoS_2

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Department:

SYNTHESES AND X-RAY INVESTIGATIONS WITHIN THE SYSTEM FeS_2-CoS_2

BY

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A

THESIS

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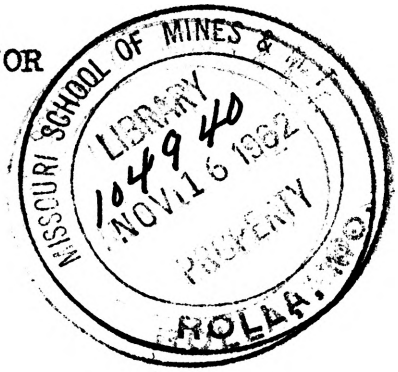

Approved by

(advisor)

ABSTRACT

Pyrite (FeS_2), cattierite (CoS_2), and various transitional members of the solid solution compounds were prepared. The methods used are as follows:

First, sulfides of cobalt, iron, or cobalt-iron were obtained by precipitation from a mixture of the cobalt chloride and/or ferrous sulfate in an aqueous solution. The dried precipitates were then mixed with an equal weight amount of sulfur and placed into silica glass tubes. After evacuation, they were filled with hydrogen gas of 3/4 of atmospheric pressure and sealed. The samples were then heated up to 500°C (for FeS_2), 650°C(for FeS_2-CoS_2), and 750°C (for CoS_2) for 24 to 72 hours. Pyrite, solid solutions of FeS_2-CoS_2, and cattierite were then formed.

In addition, pyrite has also been synthesized by using the method of WÖHLER (1836). This method is based on the direct reaction of S with Fe_2O_3 which are mixed in certain proportions and placed in an electric furnace at a constant temperature of 360°C. An amount of NH_4Cl equal to that of Fe_2O_3 + S was also added to the mixture before heating. The time of heating was between 24 to 72 hours. The pyrite crystals so produced appeared as cubes, octahedra, pyritohedra and as their combinations.

The density of natural pyrite could be changed through mechanical grinding. The finer the sample was ground the lower the density was. Therefore, the ratio of Fe to S

changed from 1:1.994 to 1:1.945. This was calculated from the equation: $nM=n(A + xB) = N_oVd$, where n is the theoretical number of atoms per unit cell (=4), A and B are atomic weights of elements in solid solution, N_o is the Avogadro's number, V is the volume of the unit cell, and d is the density. Or, the number of atoms per unit cell, varied from n' = 3.993 to n'=3.941 assuming that molecular weight is exactly FeS_2(calculated from the same equation: $n \leftarrow VdN_o/A$).

Experiments on the detection of the decomposition of pyrites have also been made by using the X-ray diffraction method. The pyrites decomposed completely into pyrrhotite and sulfur at 625°C in a vacuum; however, the decomposition started well below 625°C e.g. at 400°C.

The average lattice parameter of synthetic pyrite (5.40762 kX at 25°C) was slightly higher than that of the natural pyrites (5.40651 kX at 25°C). Yet, the linear thermal expansion coefficients of synthetic pyrite (average= 7.26×10^{-6} deg^{-1}) did not differ much from those of the natural ones (8.52 to 9.25×10^{-6} deg^{-1}) in spite of the variable crystal habit and the diverse localities of occurrence of the natural pyrites (cubes, pyritohedra, and octahedra of pyrite from the U. S., and Peru were used).

The average lattice parameter of synthetic cattierite (CoS_2) was 5.52508 kX at 25°C and the average linear thermal expansion coefficient was 13.76×10^{-6} deg^{-1}.

The components FeS_2 and CoS_2 formed a complete series of solid solutions at 650°C and the lattice parameter changed along a straight line from that of FeS_2 to that of CoS_2.

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CHAPTER I
INTRODUCTION

Pyrite is the most common sulfide mineral in the crust of the earth, and is found in practically all types of rocks. Although the ideal chemical composition of pyrite is FeS_2, cobalt and nickel can substitute for iron; thus, cobaltian, or nickelian pyrite, and bravoite occur in nature.

According to BERRY & MASON, (1959), the substitution of Ni for Fe causes an increase in the lattice parameter of the cubic unit cell. Their data were obtained from the measurement of natural bravoite and synthetic NiS_2.

As to the substitution of Co for Fe, there was very little experimental information available when the present thesis work was started. Recently, KLEMM, (1962), reported on a fairly complete ternary FeS_2-NiS_2-CoS_2 study.

The purpose of this work was to find out proper methods of producing artificial pyrites, cobalt disulfides, and solid solutions of FeS_2-CoS_2, and to measure the lattice parameters, linear thermal expansion coefficients, and densities of both natural and artificial pyrites, of artificial cobalt disulfides, and of FeS_2-CoS_2 solid solutions, by means of X-ray diffraction.

Pyrite is the stable form of iron disulfide. In an ideal case, pyrite should have the iron-sulfur ratio of 1:2. Therefore, $FeS_{2.0}$ is considered to be a standard molecular formula for pyrite although the iron-sulfur ratio actually

varies from sample to sample in nature.

According to PAULING (1945), pyrite has a covalent bond structure. It belongs to the AX_2 type of structure where A corresponds to the iron atom and the X_2 may represent sulfur atoms, as well as Te, Se, Sb, or As(BERRY & MASON 1959).

The iron atoms of pyrite are in the arrangement of a face-centered cubic lattice and are in a sixfold coordination with sulfur atoms. The sulfur atoms occur in pairs which lie along the trigonal direction of the lattice. The sulfur pairs are also coordinated to six iron atoms (BRAGG, W.L. 1920).

A sketch of the structure of pyrite, according to EROR & WAGNER, 1962, is shown in Figure 1.

Pyrite, as a crystal of the cubic system with symmetry $2/m\ \bar{3}$, commonly occurs as cubes (100), pyritohedra (210) or octahedra (111), also as trapezohedra (112) and diploids (321). It is not uncommon that pyrite shows combinations of the above mentioned forms or as twin after the "Iron Cross Law" (twin axis 110, interpenetrating). Figure 2 shows some typical habits of pyrite. Crystals of CoS_2, NiS_2, MnS_2, etc. also occcur in the same type of structure as FeS_2 does.

ELLIOTT, 1960, has re-examined the crystal structure of FeS_2, CoS_2 and NiS_2 and found out that the sulfur-sulfur distances are not equal, they depend on the number of anti-bonding electrons shared with the metal ions.

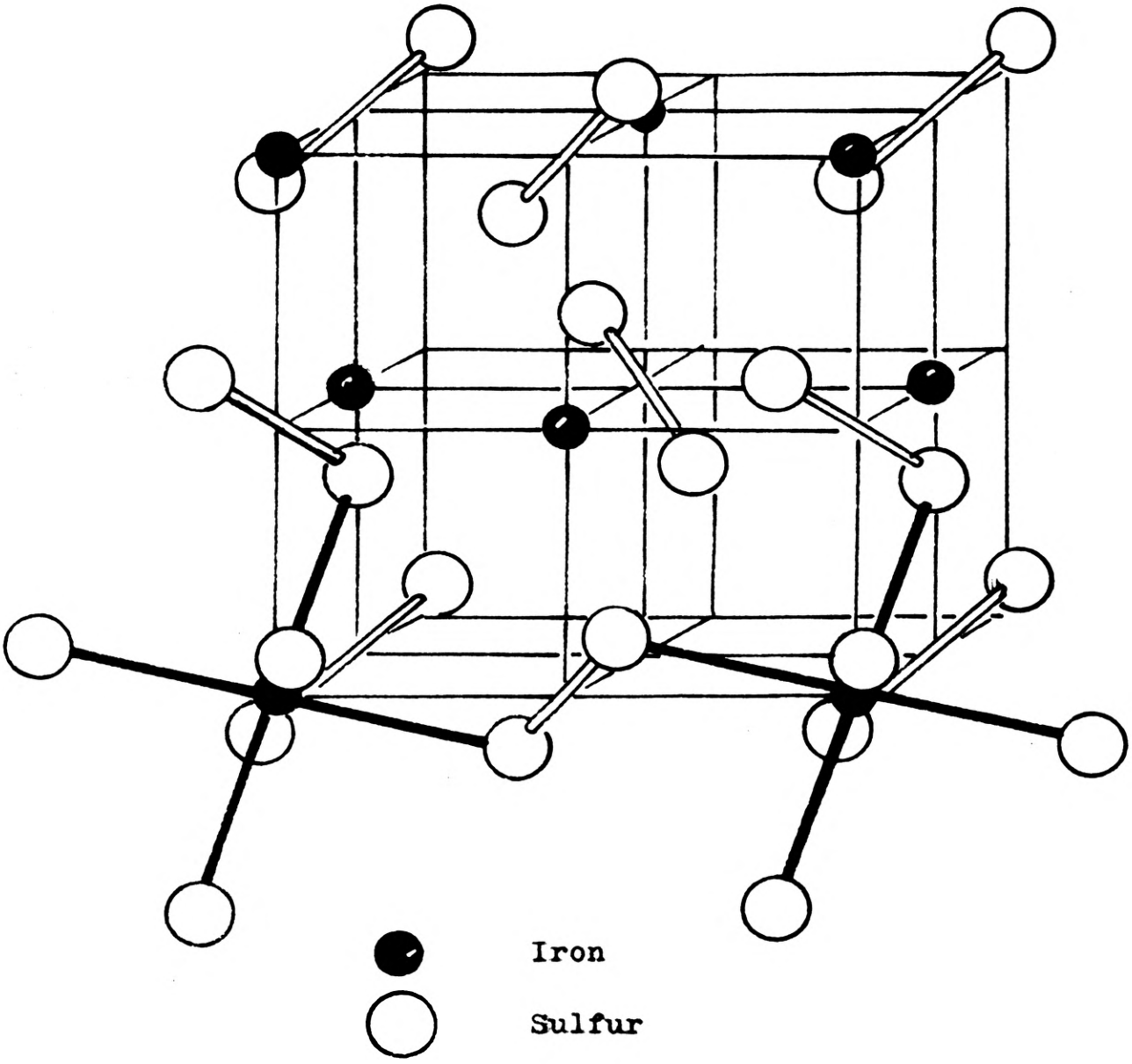


Figure 1

Structure of Pyrite

(after N.G.EROR & J.B.WAGNER,Jr.)

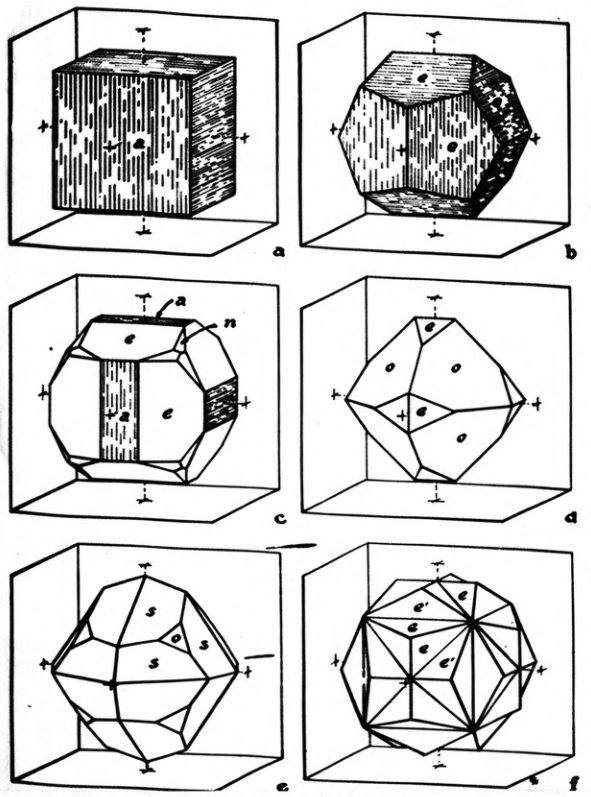


Figure 2

Pyrite crystals. Forms: cube a (100), pyritohedron e (210), octahedron o (111), trapezohedron n (112), diploid s (321). (f) Pyritohedron e (210) in twinned position e', twin axis (110), Iron Cross Law. (a), (b), and (c) show the common striations on cube and pyritohedral faces.

(After L.G.BERRY & B,MASON, 1959, Fig.9-21,p.329)

CHAPTER II
REVIEW OF LITERATURE

A. Synthesis of Pyrite.

Pyrite has been made artificially by means of various methods under various conditions by many investigators. Of these descriptions only a few syntheses of pyrite will be mentioned here.

Early in 1836, WÖHLER briefly described a method of synthesis of pyrite, using Fe_2O_3, S, and NH_4Cl as reactants. The procedure, the temperature-pressure conditions, and the duration of heating were not described.

EATON, HYDE & ROOD (1949), made radioactive pyrite by filling the aqueous solutions of sodium sulfide, radioactive sulfur, and iron sulfate into a stainless steel bomb (which was sealed subsequently) and by heating of the bomb for 7 days at 250°C.

ROSENQVIST, (1954), prepared artificial pyrite from iron and sulfur. The iron was carbonyl iron which had been treated with hydrogen at 700°-900°C in order to remove the surface oxides. The pyrites were prepared by heating the mixtures of iron and sulfur powder in evacuated and sealed Pyrex glass tubes at 500°-600°C for a day or two.

ROSENTHAL, (1956), grew pyrite from ferric chloride solution by saturating it with H_2S at room temperature. It took 14 days to prepare crystaline pyrite powder.

KULLERUD & YODER, (1959), used both rigid silica glass tubes and collapsible gold tubes for the preparation of artificial pyrites. They also used iron and sulfur as reactants. They mixed the iron and sulfur powder first in the ratio of 1:1 and held it at 550°-600°C in closed silica tubes for one week to form troilite. Sulfur was then mixed with troilite to form pyrite.

KLEMM, (1962), again used iron and sulfur powder and mixed it with LiCl-KCl, which produced pyrite when melted. The mixtures of Fe, S, LiCl and KCl were heated at temperatures of 500°C, 600°C and 700°C. The time of heating was 100 hours in all cases.

B. Synthesis of Cobalt Sulfides.

Among all the sulfides of cobalt, only the cobalt disulfide (CoS_2) has the same crystal structure as pyrite. In order to investigate the solid solubility of FeS_2 and CoS_2, the synthesis of CoS_2 was necessary. Yet, there are only a few descriptions concerning this matter in the literature.

According to a letter of Dr. ROSENQVIST, (1962), CoS_2 can be produced in the following manner (quotation from the letter):

" The procedure we used was first to prepare some CoS by synthesis from the elements in evacuated and sealed silica tubes at about 750°C for 25 hrs. This material was ground finely and mixed with additional sulfur to make CoS_2 ... We used three heatings where the temperature was gradually increased from 630°C to 780°C and with a total duration of 125 hrs..."

KLEMM, (1962, p.37), produced CoS_2 in a similar manner as used for the synthesis of pyrite. He put the mixtures of cobalt powder, sulfur, and LiCl-KCl into Pyrex glass tubes, evacuated and sealed them. These mixtures were heated to 400°C for 50, 160, and 500 hours.

C. X-ray Investigation of Natural Pyrite.

The determination of the crystal structure of natural pyrite by means of X-ray diffraction was done by many investigators. Lattice parameters were also measured. A summary of lattice parameters obtained for natural pyrites by different persons is given in Table I.

However, the precision of most of these measurements is questionable due to the lack of temperature control. On the other hand, impurity elements in the crystal lattice of natural pyrites could also have been the reason for the variation in their lattice parameters.

D. Composition and Decomposition of Natural Pyrite.

1. Chemical Composition of Natural Pyrite

BUERGER, (1934), reviewed the data of the chemical analyses of natural pyrites and stated that the composition of pyrite corresponds closely to ideal FeS_2.

SMITH, (1942), made some analyses and stated that the position of pyrite varied from sample to sample. The ratio of iron to sulfur varied from 1:2.01 to 1:1.94. He believed that the deficiency in sulfur is caused by structural imperfection of the pyrite crystals.

TABLE I

Lattice Parameters of Natural Pyrites

Year of Publication	Name of Investigator	Lattice Parameter (in Angstrom)
1913	BRAGG, W.L.	5.404
1920	BRAGG, W.L.	5.39
1925	RAMSDELL, L.S.	5.38
1927	De JONG, W.F.	5.403 ± 0.003
1928	AMINOFF, G. & PARSONS, A.L.	5.40
1928	OFTEDAL, I.	5.414 ± 0.003
1932	BRADLEY, A.J.	5.405
1932	BANNISTER, F.A.	5.40
1932	PARKER, H.M. & WHITEHOUSE, W.J.	5.405
1933	ANDERSON, H.V. & CHESLEY, K.G.	5.40
1938	BOLDYREW, A.K.	5.416
1938	HANAWALT, J.D.	5.42
1940	HANNISTER, F.A.	5.402
1941	PEACOCK, M.A. & SMITH, F.G.	5.4079 ± 0.0005 5.4063 ± 0.0005
1942	HARCOURT, G.A.	5.54
1945	KERR, P.F.; HOLMES, R.J. & KNOX, M.S.	5.40667 ± 0.00007
1951	GORDON, R.B.	5.4179 ± 0.0003
1955	SWANSON, H.E.	5.417
1960	ELLIOTT, N.	5.404

KULLERUD & YODER, (1959), again reviewed critically the chemical analyses of natural pyrites and concluded: "This review of the evidence strongly suggests that variations in the metal-to-sulfur ratio of pyrite are occasioned by inadequate analytical techniques, impure samples, or both."

2. Decomposition of Natural Pyrite

Only a few extensive studies on the subject of decomposition of pyrite have appeared in the literature. ROSENQVIST, (1954), did some experiments on this subject when he studied the Fe-S system. KULLERUD & YODER, (1959), studied the decomposition of pyrite in detail as indicated in their publication on the stability of pyrite.

Table No. II lists all the data found on the decomposition of pyrite.

E. X-ray Investigation of Synthetic Pyrite.

Synthetic pyrites, as has been mentioned in the previous section, were prepared by many methods by many investigators. However, accurate X-ray diffraction work has not been done on synthetic pyrites until the very recent years.

SWANSON, (1955), prepared his artificial pyrite from the heating of FeS_2 precipitates in a sulfur atmosphere at 700°C for 4 hours. The lattice parameter of this artificial pyrite was determined to be 5.417Å.

LEPP, (1956), made precise measurements of the lattice parameters of his synthetic pyrites and stated the average value to be 5.4176 ± 0.0003 Å.

TABLE II

Decomposition of Pyrite

Pyrite=pyrrhotite + liquid of gas of sulfur

Year of Publication	Name of Investigator	Temp. of Decomposition (°C)	Remarks
1898	CUSACK,R. (KULLERUD&YODER, 1959)	642	decomposed suddenly.
1911	KOTHNY, E. (KULLERUD&YODER, 1959)	700	dissociation began at 200°C
1912	HEMPEL,N.&SCHUBERT, C.(KULLERUD&YODER, 1959)	480	
1942	JENSEN, E. (KULLERUD&YODER, 1959)		"pyrite and pyrrhotite formed a eutectic at about 1000°C."
1954	ROSENQVIST, T.		"at 800°C, pyrite would undergo a peritectic decomposition to give pyrrhotite and liquid sulfur.
1959	KULLERUD,G. & YODER, H.S.	743 748 755 770 810	(at 10 bars) (at 335 bars) (at 1000 bars) (at 2000 bars) (at 5000 bars)

KULLERUD & YODER, (1959), obtained an average value for their synthetic pyrites as 5.419 ± 0.002 Å.

None of these measurements were made under temperature control.

F. X-ray Investigation of Cobalt Sulfides.

HULSMANN & BILTZ, (1935), made an interesting comparison of X-ray diffraction data in cobalt sulfides (CoS, $CoS_{1.09}$, $CoS_{1.23}$; $CoS_{1.39}$, $CoS_{1.58}$, $CoS_{1.69}$, $CoS_{1.85}$, and $CoS_{1.98}$). The last reflection plane in CoS was 322, and in $CoS_{1.98}$ was 521.

In LUNQVIST & WESTGREN'S paper (1938), the lattice parameter of CoS_2 was determined to be 5.524 Å, whereas De JONG & WILLEM'S data for the lattice parameter of CoS_2 was 5.64 Å.

HEIMBRECHT & BILTZ, (1939), investigated the reaction of $Co_3S_4 = 2CoS + CoS_2$, and studied the mixture of $CoS-CoS_2$ by means of X-ray diffraction. Yet, no direct comparison of their results and the X-ray data for CoS_2 studied by other investigators was made.

KLEMM, (1962a), datermined the lattice parameter of CoS_2 to be 5.537 Å.

In conclusion, from this review it is evident that extensive work has already been done on the synthesis and on structural properties of pyrite. However, information concerning the synthesis and X-ray work on CoS_2 and on solid solutions of FeS_2-CoS_2 is very limited. Therefore, the present thesis is trying to fill this gap. This is also true for the present investigation of the expansion coefficient of CoS_2.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. Synthesis.

1. Synthesis of FeS_2 (pyrite)

The three conditions for the synthesis of pyrite in the present study were, a short period of formation, a simple procedure, and the yielding of a satisfactory quantity of the crystallized product. For this reason, WÖHLER's dry melt method was first applied. By this method, only three kinds of chemical reagents were needed: sulfur, powder of Fe_2O_3, and NH_4Cl, all of commercial purity.

WÖHLER did not mention the proportion of the reactants he used, nor the procedure in detail. However, through trial and error, pyrites were made by the writer in the following manner, sulfur, Fe_2O_3 and NH_4Cl were well mixed in a weight ratio of 3:1:1, and were put into a Pyrex tube of 30 cm in length, 1.5 cm in width. The Pyrex tube was evacuated and sealed, since with open flask it was difficult to produce any pyrite, therefore, the glass had to be sealed. The tube, with the mixed components inside, was put into a hot electric furnace of the resistance type. The temperature of the furnace was held constant at 360°C through the whole period of heating by a controller. After 48 hours of heating, the tube was taken out immediately from the furnace. The sample inside the tube was thus air quenched from 360°C to room temperature within a few minutes.

The excess sulfur was removed by extraction with CS_2. The remaining NH_4Cl could be dissolved in distilled water. The unreacted Fe_2O_3 and glass splinters were separated mechanically. Finally, a yellowish coarse crystalline powder was left which by X-ray investigation turned out to be pyrite.

The NH_4Cl used in the synthesis of FeS_2 may act as a kind of catalyst and also as an inhibitor for the prevention of the re-oxidation of iron (if open air synthesis is used).

The overall reaction between sulfur and iron oxide may be as follows:

$$2Fe_2O_3 + 11S \rightarrow 4FeS_2 + 3SO_2$$

WÖHLER's method, however, was not considered by the writer to be too satisfactory because of three reasons: First, the procedure was not the most simple one; second, the reproducibility was poor; third, explosion occurred too often. However, good crystals were occasionally obtained. Nevertheless, another method was also used by the writer.

The second method used to produce FeS_2 consisted of a precipitation from hot. dilute solutions of ferrous sulfate ($FeSO_4$ $7H_2O$) by ammonium polysulfide. Very fine grained, black precipitates of iron sulfides were obtained immediately. After approximately 20 minutes of boiling, all the black precipitates of the iron sulfides settled

on the bottom of the flask. The precipitate was washed by decantation with distilled water and then filtered under pressure. The precipitates were dried and were examined by means of X-ray diffraction. The X-ray pictures showed that the product was not FeS_2. Therefore, sulfur powder was added in excess to these iron sulfides (in a weight ratio of 1:1). The mixture was put into a silica glass tube of 1.5 cm in diameter. After evacuation, 3/4 of atmospheric pressure of hydrogen gas was filled into the tube. The tube was then sealed. The purpose of filling hydrogen gas was to reduce the oxygen layer on the sulfide particles to further the reaction during heating. The sealed tube was then placed into an electric furnace which was preheated up to 600°C. The heating treatment was continued at a constant temperature of 600°C for 24 hours. Finally, the tube was air quenched by taking it out of the furnace. The sulfide was now available for investigation by X-ray diffraction. The pattern of pyrite was obtained.

2. Synthesis of CoS_2

Cobalt disulfide (CoS_2), according to the literature has pyrite structure (WYCKOFF, 1909). In order to investigate the mutual solubility between pyrite and cobalt sulfides, naturally the first attempt was to produce CoS_2 because the natural CoS_2 is extremely rare and impure. (KERR, 1945; RAMDOHR, 1960).

Cobalt(ous) Chloride ($CoCl_2.6\ H_2O$) was dissolved in

distilled water, and heated. Then, diluted ammonium polysulfide solution was added. Black precipitates of cobalt sulfide(s) appeared at once. The solution was made slightly acidic by adding diluted HCL in order to obtain better precipitation. The precipitates were washed as already described (in the section on FeS_2), and dried. By X-ray diffraction it was found that the black precipitate was not CoS_2. Therefore, these cobalt sulfides were mixed with sulfur in a weight ration of 1:1, put into a silica glass tube, evacuated and partially filled with H . After sealing the tube, the sample was heated to 750°C for 24 hours and air quenched. The sulfide obtained showed an X-ray pattern of pyrite.

Therefore, this was CoS_2, as the lattice parameter also agreed with the value given in the literature.

Another method was also tried for the synthesis of CoS_2: cobalt and sulfur, both in powder form, were mixed in various proportions, were put into the silica tubes which later were evacuated, filled with H_2, and then heated at 600° and 800°C at various rates in different experiments. Unfortunately, the X-ray photographs of the reaction products did not show the CoS_2 pattern, this being in contradiction with the experiments of other authors. It is possible that the grain size of the original components was too coarse.

3. Synthesis of FeS_2-CoS_2 Solid Solutions

Synthetic FeS_2 was mixed with small amounts of synthetic CoS_2, and the mixture was put into silica glass tubes which were then evacuated, filled with hydrogen gas and sealed. Most of the samples were heated to 600°C for 48 hours. X-ray phtographs and lattice parameters did not differ significantly from those of the pure pyrites. Therefore, it must be assumed that under such conditions the CoS_2 could not go into the structure of FeS_2 forming a solid solution.

For the above mentioned reason, the method of coprecipitation was used in order to obtain FeS_2-CoS_2 solid solutions. Ferrous sulfate and cobalt(ous) chloride were the sources of Fe and Co for the coprecipitation. At first, gravimetric analyses of the solutions were made to determine the concentrations of Fe^{2+} and Co^{2+} in them. The quantities of CO^{2+} were determined in the following manner (F.P. TREADWELL, 1909): Cobalt(ous)chloride ($CoCl_2.6H_2O$) solution was evaporated completely through slow heating in a crucible. H_2SO_4 was added which lead to the formation of $CoSO_4$. $CoSO_4$ was ignited until the crucible was red hot. After cooling, the dry $CoSO_4$ was weighed and the amount of Co^{2+} calculated simply by using the following equation:

Wt. of $CoSO_4$: Wt. of Co = Mol.Wt.of $CoSO_4$: At.Wt.of Co

The amount of Fe^{2+} in the solution was determined by deposition of $Fe(OH)_2$, oxidation by bromine to $Fe(OH)_3$, Drying and heating the deposits Fe_2O_3 was weighed.

After knowing the exact concentration of the ferrous sulfate and of the cobalt(ous) chloride prepared, aqueous solutions of desired molarities could be obtained by dilution. Then, a calculated amount of ferrous sulfate solution and of cobalt(ous) chloride solution measured by a pair of burettes were mixed in certain proportions. The mixed solution was then heated until boiling and diluted ammonium polysulfide solution was added. Black sulfide precipitations were formed at once. After washing, filtering, and drying, the residue (iron and cobalt sulfides) was checked by X-ray diffraction. As the X-ray picture did not show the pyrite structure, the precipitate was mixed with sulfur powder in a weight ratio of 1:1, and was put into a silica glass tube. The tube was then evacuated, filled with hydrogen gas, and sealed. The sample was now heated at 600°C for 24 hours, and was air quenched by taking it out of the furnace. The product was then checked again by the use of X-ray diffraction. A pattern belonging to a pyrite structure was obtained.

B. X-ray Investigation.

1. Selection and Description of the Method

For three main reasons the writer applied X-ray diffraction to the present investigation:

First, using the technique of X-ray diffraction for the identification of minerals and chemical compounds, in forms of powder, was considered to be simple and effec-

tive.

Second, the change of lattice parameters of a crystal due to the change of temperature could best be measured on X-ray diffraction lines.

Third, the substitution of Co for Fe inside the crystal lattice of pyrite, or Fe for Co in case of cattierite, is expected to be accompanied by a change in the lattice parameter.

Various methods of X-ray diffraction are available. In this present work, the selection of one of the most precise methods was very essential. Since the synthetic FeS_2, CoS_2, and FeS_2-CoS_2 occured mainly as very fine grained powders in small amounts, it was better to use a powder method.

For these reasons, the asymmetric method was selected for the precision determination of the lattice parameters. The main principles of this method are as follows:

(a) The X-ray film is placed inside a precise cylindrical camera in such a manner that the ends of the film are at an angle of 90° with respect to the incident X-ray beam. In this way, the exact entrance point and exit point of the X-ray beam can be determined from measuring the symmetrically occurring diffraction lines (or rings) around these points. As there is 180° between them, the effective film circumference can be accurately calculated in spite of the shrinkage of the film. The reflection angle in mm can be determined directly from

the film, and by multiplication with a factor calculated from the film circumference it can be converted into degrees.

(b) In the asymmetric method, the distance between the identical last diffraction rings on the film are the only ones that have to be precisely measured for the precise calculation of the lattice parameters, if the film circumference is known. This is due to the fact that the absorption error vanishes in the high reflection region and may affect the lattice parameter by only one or two parts in the fifth decimal place.

(c) For precise lattice parameter determination the exact centering of the sample, the fineness of the grain size of the sample, and the diameter of the glass fiber are of great importance. Therefore, a precisely built camera with accurate adjustment for centering is necessary; a fine grained sample is preferable, the optimum grain size being between 10^{-3} and 10^{-4} mm; the optimum diameter of the fiber of LINDEMANN glass is about 0.08 mm; and the overall cross-section of sample and glass fiber together should be in the neighborhood of 0.2 mm in diameter.

2. Determination of Lattice Parameters

The determination of lattice parameters was actually the basic part of the X-ray investigation of the present thesis. A brief description of it is therefore given in the following paragraphs.

According to the BRAGG equation:

$$\lambda = 2d\sin\theta$$

where $d = a / (h^2 + k^2 + l^2)^{\frac{1}{2}}$

Hence $a = \lambda(h^2 + k^2 + l^2)^{\frac{1}{2}} / 2\sin\theta$

Where a is the lattice parameter

λ is the wavelength of the characteristic X-radiation

θ is the BRAGG diffraction angle and

(h,k,l) are the X-ray indices

Therefore, lattice parameters of FeS_2, CoS_2, FeS_2-CoS_2 crystals can be obtained from this calculation since the wavelength of the radiation of the target material is known from handbooks, the BRAGG angle can be calculated from the measurement of X-ray powder patterns, and the planes of reflection can be found by graphical indexing of this pattern. An example of measurement and indexing of the cubic CoS_2 pattern is given below.

(a) Film measurement

Chromium radiation was used in the above mentioned example (wavelength of chromium radiation: $K_{\alpha_1} = 2.28962$ Å , $K_{\beta_1} = 2.08480$ Å). In order to obtain the values of the BRAGG angles, the circumference of a film had to be determined first, from the readings of the front reflection and the back reflection lines, using a comparator. A factor calculated from the measurement of film circumference was then used for conversion of the angles expressed in millimeters into degrees.

(b) Indexing

Knowing the θ angles a graphical method (STRAUMANIS, 1952) was used to find out the indices of the powder lines. A sphere of reflection, 20cm in diameter, corresponding to the inner wall of the cylindrical camera was drawn (figure 3). The 2θ angles were marked on the sphere of reflection and the radii projected on the diameter of the circle of figure 3. The unit length of these projections was in proportion to the reflection plane Σh^2 (in integers 1, 2, 3, ...). Therefore, the indices of these powder lines can easily be found.

(c) Calculation of a Lattice Parameter

After indexing, the calculation of lattice parameters can ~~now~~ be made. For the precise lattice parameter calculation, only the last ring of the back reflection region was needed. However, in this example, this ring was produced by the Cr.-K_β radiation. The index of this reflection was determined as follows: knowing the lattice parameter of CoS_2 calculated from the last α_1 interferences and using the BRAGG equation,

$$a = \lambda(h^2 + k^2 + l^2)^{\frac{1}{2}} / 2\sin\theta$$

or $$(h^2 + k^2 + l^2)^{\frac{1}{2}} = 2a\sin\theta a/\lambda$$

the index of this last ring produced by the Cr.-K radiation can now be found. By the use of the index of this last ring, the precision lattice parameter of CoS_2 was finally obtained.

TABLE III

An example (CoS_2) for film measurement and calculations is given below:

Film No. 2027 Composition CoS_2 Temp. 25°C Radiation: Cr.

Average Reading: (in Front) 120.343 (in back) 320.141 Time of Exposure: 1 hour

Film Circumference: 320.141-120.343 = 199.798

Conversion factor: $F = \frac{90}{199.798} = 0.450455$

Reading (in mm)	79.577 / 40.828	83.563 / 36.777	87.395 / 35.965	180.721 / 139.449	175.648 / 144.490	173.271 / 146.877
Sum(in mm)	120.405	120.340	120.360	320.170	320.138	320.148
Difference (in mm)				41.272	31.158	26.294
4θ mm	38.749	46.786	54.430	158.521	168.640	173.404
θ°	17.455	21.075	24.518	71.407	75.965	78.111
2θ°	34° 55'	42° 09'	49° 02'	135° 21'	151° 56'	156°13'

Sinθ 0.978549

$\sqrt{\Sigma h^2}$ 27

$\frac{1}{2}\lambda\sqrt{\Sigma h^2}$ 5.40644 kX

a 5.52496 kX

Remark: The integer number of the unit length of the last , reflection line was 22. But the integer number of the last ring was uncertain, and had to be determined. This could be done only by trial and error. The value of the lattice parameter of CoS_2 obtained from the measurement of the last , line was used, from the BRAGG equation, the integer number of the last ring of CoS_2 was then found to be 27, (3, 3, 3).

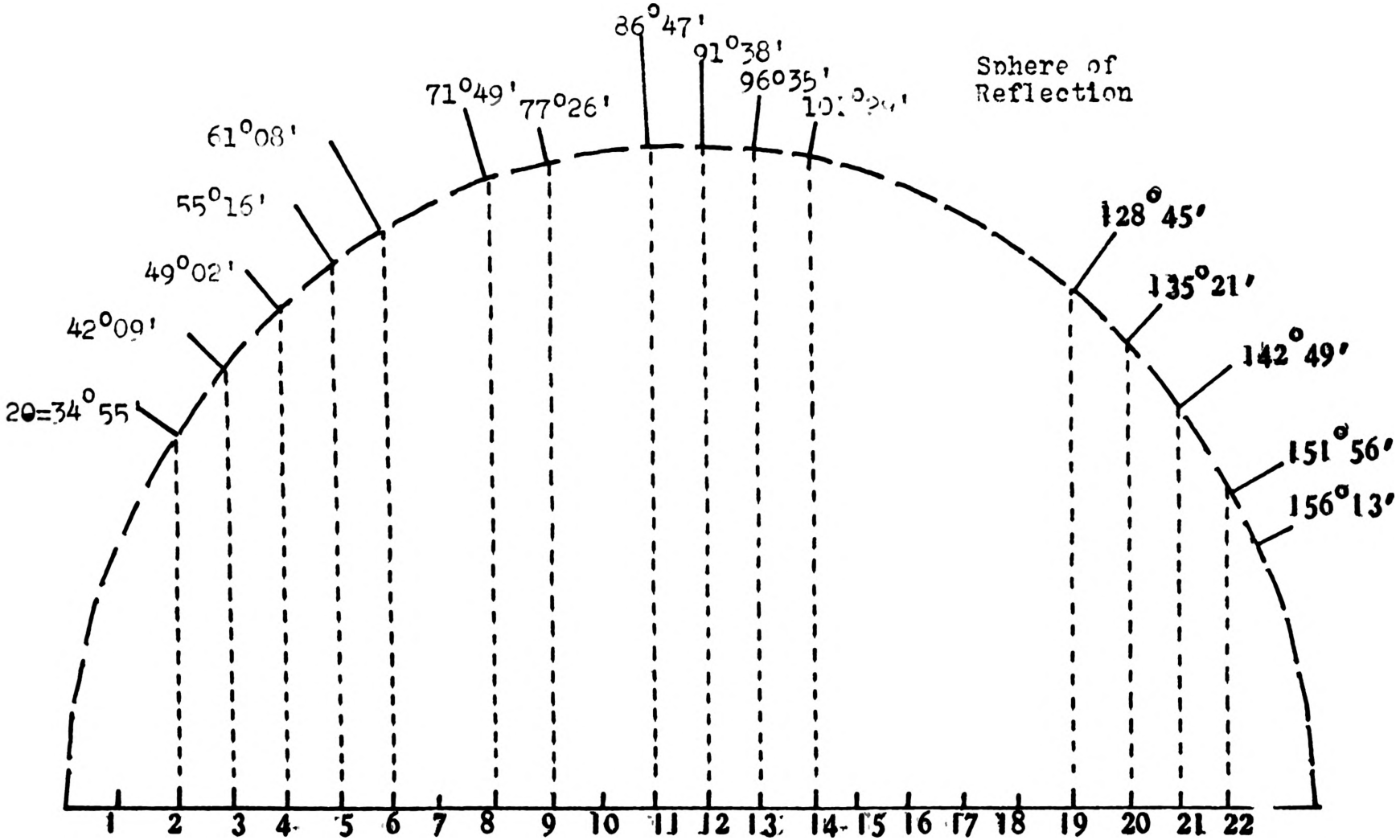


Figure 3

Graphical Indexing of the Powder Pattern of CoS_2

3. Determination of Thermal Linear Expansion Coefficients.

The lattice parameter of a crystal varies with the temperature. The magnitude of variation of lattice parameters depends mainly on the thermal linear expansion coefficient of the crystal. Therefore, thermal linear expansion coefficients can be calculated from lattice parameters measured at various constant temperatures. The definition of the thermal expansion coefficient α is as follows:

$$\alpha = a_{t_2} - a_{t_1} / a_{t_1} (t_2 - t_1)$$
$$= \Delta a / a \Delta t$$

Where a_{t_1} and a_{t_2} are the lattice parameters at temperatures t_1 ($^{\circ}C$) and t_2 ($^{\circ}C$) respectively.

In reducing the lattice parameters obtained at various temperatures to 25°C, the following equation, derived from the definition of the thermal expansion coefficient, is used:

$$a_{25} = a_{t_1} = a_{t_2} \left[1 + \alpha (t_2 - t_1) \right]$$

Where a_{25} is the lattice parameter at 25°C

a_{t_2} is the lattice parameter at temperature t_2

t_1 is 25°C

t_2 is the temperature during exposure

α is the thermal linear expansion coefficient

In this investigation, the thermal linear expansion coefficients of FeS_2, FeS_2-CoS_2 were calculated from X-ray pictures which were taken within a range of constant temperatures between 10.0°C and 65.0°C.

The experiments were done by using an X-ray thermostat which was capable of maintaining constant temperatures to an accuracy of within $\pm$ 0.02°C.

4. Density Determination

Accurate density determinations of natural and synthetic pyrites are necessary in order to calculate the number of molecules per unit cell.

A modification of the method of BAKER AND MARTIN, (1943), based on ARCHIMEDES' principle was chosen. The weight of a pyrite grain in air is different from the weight of the same pyrite when weighed in liquid. The density of it can be calculated from this difference.

The procedures of experiments were as follows:

(1) Either pyrite powder or pyrite fragments were used. Tests showed that pyrite does not dissolve in toluene.

(2) First, the weight of the pyrite fragment was obtained; the weight of the small beaker and platinum wire with the sample in air was then measured. The last step was to obtain the weight of the small beaker with the platinum wire and the sample in toluene. The operation could be repeated only after the complete evaporation of the toluene on the surfaces of the sample and the container.

(3) When pyrite powder was used as a sample, the order of weighing was somewhat different. First of all, toluene and pyrite powder were mixed. And, by the application of a vacuum, the mixture was well outgased. The first weighing was done while the powder sample and the small beaker were immersed completely in toluene. After the complete evaporation of toluene, the second weighing of the dry sample, small beaker, and platinum wire was made in air. The weights of the small beaker and the platinum in air and in toluene were obtained later.

According to BAKER & MARTIN, (1943), the density of pyrite can be calculated from the equation:

$$d = (d_1 - dg)\ (b - c)/(b - c)-(a - z) + dg$$

Where:

d, is the density of sample at $t^{o}C$.

d_1, the density of toluene at temperature $t^{o}C$.

d_g, the density of air at temperature $t^{o}C$ and pressure of the balance room.

c, the weight of small beaker and platinum wire in air.

z, the weight of small beaker and platinum wire immersed in toluene at temperature $t^{o}C$.

a, the weight of small beaker, platinum wire and pyrite immersed in toluene at temperature $t^{o}C$

b, the weight of small beaker, platinum wire and pyrite in air at room temperature.

In the case of using pyrite fragments, the item (b-c) simply means the weight of the pyrite sample alone, in air, at room temperature.

Evaporation of toluene and the change of temperature of it might possibly affect the accuracy of weighing, therefore, care was observed in maintaining a constant level of toluene in the large beaker during weighing. The temperature of toluene, the room temperature, and the atmospheric pressure have also been carefully recorded in each experiment.

In some experiments, the variation of the temperature of toluene was too great and too fast, so that a definite reading of the weight of pyrite in toluene could not be made. In this case, curves of weights of pyrite in toluene versus the temperatures of toluene had to be made in order to obtain a definite result.

5. Determination of Atoms per Unit Cell

Based on the lattice parameter and the density of pyrite, the actual number of atoms of the sample per unit cell can be calculated according to the following equation (STRAUMANIS, et. al., 1961):

$$n' = vd\ N_o/A$$
$$= a^3 d\ N_o/A$$

where n' is the actual number of atoms or molecules of the substance per unit cell.

v is the volume of its unit cell at a certain temperature (in the case of cubic substances v is equal to a^3).

d is the density of the substance at the temperature at which a^3 was calculated. The value of this temperature is commonly 25°C.

N_o is AVOGADRO'S number (6.02403×10^{23}).

A (or M) is the precise atomic or molecular weight of the substance.

The main purpose of calculating the actual number of atoms or molecules per unit cell is for the estimation of the degree of perfection of crystals.

The theoretical number of atoms n per unit cell for ideal crystals is always an integer. A direct comparison of the values of the actual and the theoretical number of atoms per unit cell provides then the information about imperfections of the crystal: If the value of the actual number of atoms per unit cell is smaller than that of the theoretical one, there must be vacant sites inside the crystal. On the other hand, if the value of the actual number of atoms per unit cell is larger than the theoretical value, the possibility of the existence of interstitial atoms in the unit cell is great. From the magnitude of the differences the degree of imperfection of the crystal can be estimated.

In case of no difference between the n' and n the crystal is a perfect or an ideal crystal; a case which is never realized in nature!

6. Composition from Lattice Parameter and Density

Assuming that the number of molecules per unit cell is an integer, the ratio of dissimilar atoms in a compound can be calculated.

According to the equation for the calculation of atoms per unit cell (STRAUMANIS, 1961),

$$n = a^3 d\ N_o/M$$

or $$nM = a^3 d\ N_o$$

where n is the theoretical number of molecules per unit cell (in FeS_2, n =4), and M is the molecular weight of pyrite.

Assuming that A represents the atomic weight of iron, B the atomic weight of sulfur, and x the number of sulfur atoms in a pyrite molecule, the above equation can be written in the following form:

$$nM = nA + nxB = a^3 dN_o$$

$$x = (N_o A^3 d - nA)/nB$$

Therefore, the sulfur atoms as well as the ratio of iron to sulfur can be calculated.

CHAPTER IV

EXPERIMENTAL RESULTS

A. Natural Pyrite

The powder of cubes of natural pyrite from Peru (sample No. 1) was studied. A lattice parameter of 5.40648 kX (at 25°C) and a thermal linear expansion coefficient of 9.25×10^{-6} deg^{-1} were obtained (as shown in TABLE IV-a). (The exact locality of all the pyrite samples studied is listed on TABLE IV-d).

The powder of one cube of natural pyrite occurring in Mississippian limestone near St. Louis has also been studied. Its lattice parameter is 5.40642 kX (at 25°C) and the thermal linear expansion coefficients were found to be 8.69×10^{-6} deg^{-1} (as shown in TABLE IV-b).

Powder of pyritohedra of natural pyrite from Peru has also been investigated. The results were similar to those obtained from the cubes of pyrites. A lattice parameter of 5.40651 kX (at 25°C) and a thermal linear expansion coefficient of 8.32×10^{-6} deg^{-1} were found (as shown in TABLE IV-c).

The data of all these investigations are summarized in Figure 4 and in the Appendix.

B. Synthetic Pyrite

The average lattice parameter of synthetic pyrite was determined to be 5.40762 kX at 25°C, and the thermal linear expansion coefficient of it was found to be 7.26×10^{-6}

Figure 4

Lattice Parameters of Pyrites at Various Temperatures

(including synthetic and natural pyrites)

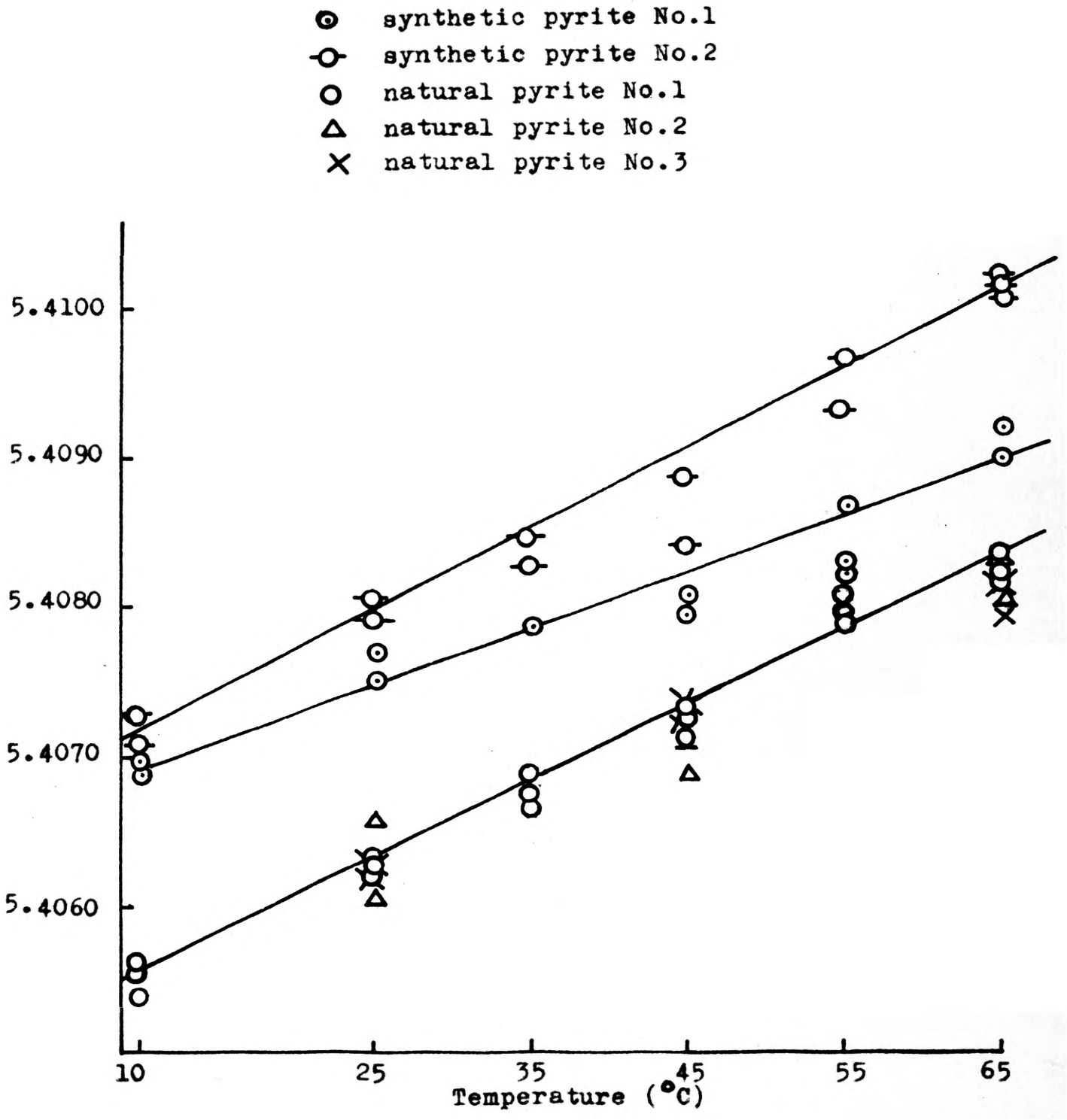


TABLE IV - a

Lattice Parameter of Natural Pyrite No. 1

Each constant is the average of three; Cr.-rad.;332 plane

Temperature (°C)	a_t (kX)	a_{25} (kX)	Thermal linear expansion coeff. (α)
10	5.40551	5.40627	
25	5.40628	5.40628	
35	5.40675	5.40626	9.25×10^{-6}
45	5.40724	5.40621	
55	5.40797	5.40651	
65	5.40826	5.40626	
		Average 5.40629	
		Refraction Corr. +0.000194	
		Lattice parameter 5.40648 $\pm$ 0.00007 kX	

TABLE IV - b

Lattice Parameter of Natural Pyrite No. 2

Each constant is the average of two; Cr.-rad.;332 plane

Temperature (°C)	a_t (kX)	a_{25} (kX)	Thermal linear expansion coeff. (α)
25	5.40632	5.40632	
45	5.40700	5.40606	
65	5.40820	5.40623	8.69×10^{-6}
		Average 5.40623	
		Refraction Corr. +0.000194	
		Lattice parameter 5.40642 $\pm$ 0.00010 kX	

TABLE IV - c

Lattice Parameter of Natural Pyrite No. 3

Each constant is the average of two; Cr.-rad.;332 plane

Temperature (^{o}C)	a_t(kX)	a_{25}(kX)	Thermal linear expansion coeff. (α)
25	5.40625	5.40625	
45	5.40736	5.40646	8.32×10^{-6}
65	5.40805	5.40625	
	Average	5.40632	
	Refraction corr.	+0.000194	
	Lattice parameter	5.40651 $\pm$ 0.00008	

TABLE IV - d

Locations of the Natural Pyrite Samples

Sample No.	Crystal Form	Locality
Pyrite 1	Cubes	Ombla Manto, Morococha, Peru
Pyrite 2	Cubes	Ste. Genevieve formation (limestone) Meramecian Series, Missis. Ft. Bellefontaine Quarry near St. Louis, Mo., U. S. A.
Pyrite 3	Pyritohedron	1200 level, Ombla Manto, Morococha, Peru
Pyrite 4	Pyritohedron	Ombla Manto, Morococha, Peru

Remark: Chromium k_{α_1}, radiation was used in all FeS_2 samples.

TABLE IV - e

Lattice Parameter of

Synthetic Cattierite

Each Constant is the average of two,

Cr. K - radiation, 333 plane

Temperature (^{o}C)	a_t(kX)	a_{25} (kX)	Thermal linear expansion coeff. (α)
15	5.52328	5.52444	
25	5.52402	5.52402	
35	5.52475	5.52468	13.76×10^{-6}
45	5.52526	5.52511	
55	5.52593	5.52570	
65	5.52683	5.52653	
	Average	5.52508	
	Refraction Corr.		
	Lattice parameter	5.52508 $\pm$ 0.00062	

Remark: The density of synthetic CoS_2 was not determined. Therefore, there is no refraction correction here.

deg^{-1} (as seen in TABLE V-a, and in Figure 4). The results of a series of studies on synthetic pyrites are also listed in TABLE V-b.

Some of the synthetic pyrite was examined under the ULTROPAK microscope and seen to consist of cubes, pyritohedra, octahedra and their combinations. Some examples are pictured in Figure 5a, b, c, and d.

C. Density Determination, Atoms per Unit Cell, and the Atomic Ratio of Fe and S in Natural Pyrite

Density determinations of large pieces, coarse grains and very fine grained powder made from solid fragments of natural pyrite No. 3 were made. The densities of pyrite ranged from 5.0020 g./cc at 25°C to 4.9369 g./cc. Nine samples have been studied, and the results are shown in TABLE VI.

The number of molecules per unit cell of pyrite was determined from the lattice parameters and from the density. The data on molecules per unit cell is also given in TABLE VI.

The atomic ratio of Fe and S was determined from the number of molecules per unit cell assuming that this number is now exactly 4.000. The results are listed in TABLE VII. The sulfur content of pyrite was decreased by mechanical grinding, as revealed by differences between experiment No. 3 and No. 9.

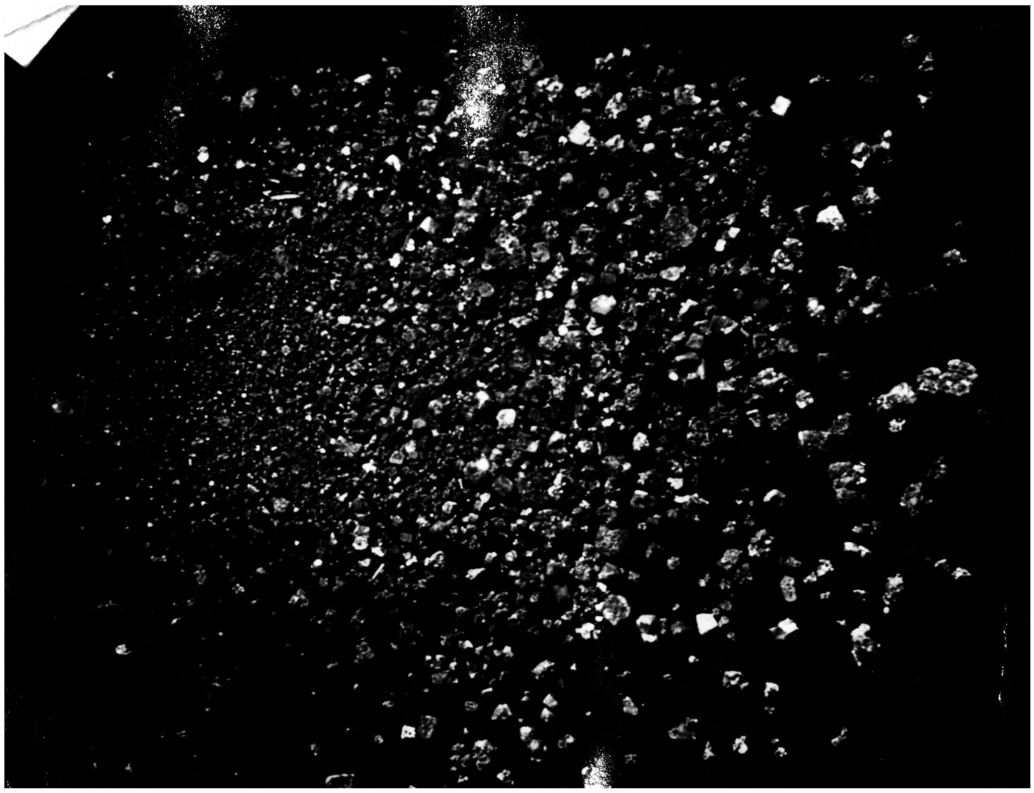


Figure 5-a

Grains of synthetic pyrite No.A-1
obtained by WÖHLER's method.
Direct one to one photograph,
enlargement 4 x linear.

Figure 5-b

Enlargement of a portion of Figure 5-a, in which cubes, cubo-octahedra and perhaps also pyritohedra of synthetic pyrite can be seen. Direct one to one photograph, enlargement 8 x linear.

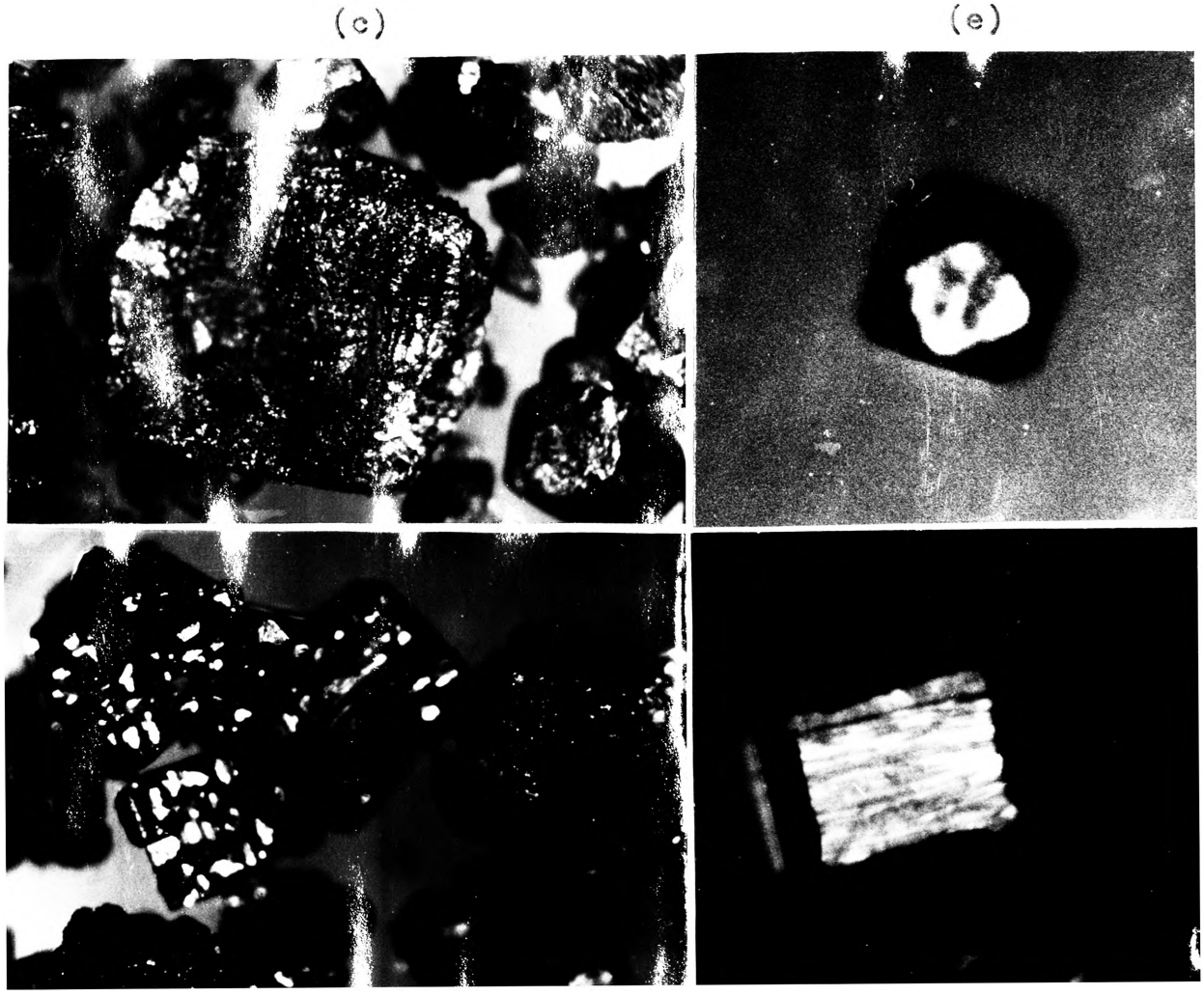


Figure 5 c,d,e,f.

Illustrations of single crystal grains and clusters of the synthetic pyrite A-1. Cubes, cubo-octahedra and probable pyritohedra all occur in one and the same synthetic product. Figure f shows irregular striations on the (100) face. Photographs taken with a 3.2 LEITZ ULTROPAK lens. Enlargement : c and d about 100 x; e and f about 300 x .

TABLE V - a

Lattice Parameter of Synthetic Pyrite No.1

Each Constant is the Average of Two; Cr.-rad.;332 plane

Temperature (°C)	a_t(kX)	a_{25}(kX)	Thermal linear expansion coeff. (α)
10	5.40700	5.40759	
25	5.40765	5.40765	
35	5.40783	5.40744	7.26×10^{-6}
45	5.40797	5.40719	
55	5.40828	5.40710	
65	5.40916	5.40759	
		Average	5.40743
		Refraction Corr.	+0.000194
		Lattice parameter	5.40762 $\pm$ 0.00049 kX

TABLE V - b

Lattice Parameters of Synthetic Pyrites
(Cr.-radiation, 332 ref. plane)

Exp. No.	Temperature (°C)	Tube Pressure (cm.Hg)	$a_{t(kX)}$	Remark
$A\text{-}3_2$	25.2	Vacuum	5.4048	Without Al-block
A -4	25.1	Vacuum	5.4052	
A-6	26.8	Vacuum	5.4043	
A-8	26.0	Vacuum	5.4061	
A-9	26.0	Vacuum	5.4083	
A-10	26.0	Vacuum	5.4063	
B-1	24.9	4.3	5.4072	Without Al-block
$B\text{-}9_2$	26.5	5.3	5.4067	
$B\text{-}10_1$	26.2	4.8	5.4076	
B-11	26.0	2.7	5.4090	
B-12	24.0	2.5	5.4076	
B-13	24.2	2.3	5.4058	
B-14	23.0	2.3	5.4072	
B-15	23.4	Vacuum	5.4066	
$B\text{-}16_2$	27.6	1.2	5.4050	
B-19	27.6	2.0	5.4056	

Remark: The values are not uniform. This is due to the fact that the X-ray patterns were blurred.

TABLE VI

Density of Natural Pyrite No. 3
and the Number of Molecules per Unit Cell

Exp. No.	Sample	Lattice parameter	Thermal exp. Coeff.	Density exp.	No. of M. per unit cell
		a_{25}(kX&A)	α(mole^{-1})	d_{25}(g./cc)	n'
D.D.-3	Crystal fragment	5.40651±0.00008kX	8.32	5.0020	3.9932
D.D.-4	"	"	"	4.9997	3.9913
D.D.-5	"	"	"	4.9996	3.9912
D.D.-6	Fine Powder	"	"	4.9580	3.9580
D.D.-7	Coarse grains	"	"	5.0012	3.9917
D.D.-8	Crystal fragment	"	"	4.9982	3.9901
D.D.-9	Fine Powder (ground from D.D. No. 7)	"	"	4.9369	3.9412

Remarks:

1. The value of each density measurement is the average of eight to twelve runs.
2. The low values of density of pyrite powder(D.D.No.6 & D.D. No.9) is apparently due to the loss of sulfur during grinding, as suggested by the sulfur ordor during crushing and grinding of pyrite.

TABLE VII

Atomic Ratio of Fe and S
in Pyrite, Assuming that n = 4.000
(natural Pyrite No.3)

Exp. No.	Sample	$N_o v$ d	x(Fe:S)
3	Crystal Fragment	479.08586	1:1.994
4	"	478.86025	1:1.992
5	"	478.84689	1:1.992
6	Fine Powder	474.86348	1:1.961
7	Coarse grains	478.90090	1:1.992
8	Crystal Fragment	478.71758	1:1.991
9	Fine Powder	472.84736	1:1.945

TABLE VIII

Lattice Parameter of Heated Natural Pyrite

(from natural pyrite No. 3, Peru; heated in vacuum), Cr.-rad., 332

Exp. No.	Time of heating (hr.)	Const. temp. of heating (°C)	Room temp. during exp. (°C)	a_t (kX)	a_{25}(kX)	a_o (kX) (after refr. correction)
N-1	72	525	22			
N-2	48	520	22	5.40614	5.40625	5.40644
N-3	24	525	23	5.40623	5.40634	5.40653
N-4	30	525	28	(FeS)		
N-5	24	625	26.6	(FeS)		
N-6	48	545		(FeS)		
N-7	48	525	24	5.40619	5.40615	5.40634
N-8	24	625	26	.(FeS)		
N-9	24	625	24.5	(FeS)		
N-10	12	625	27.7	(FeS)		

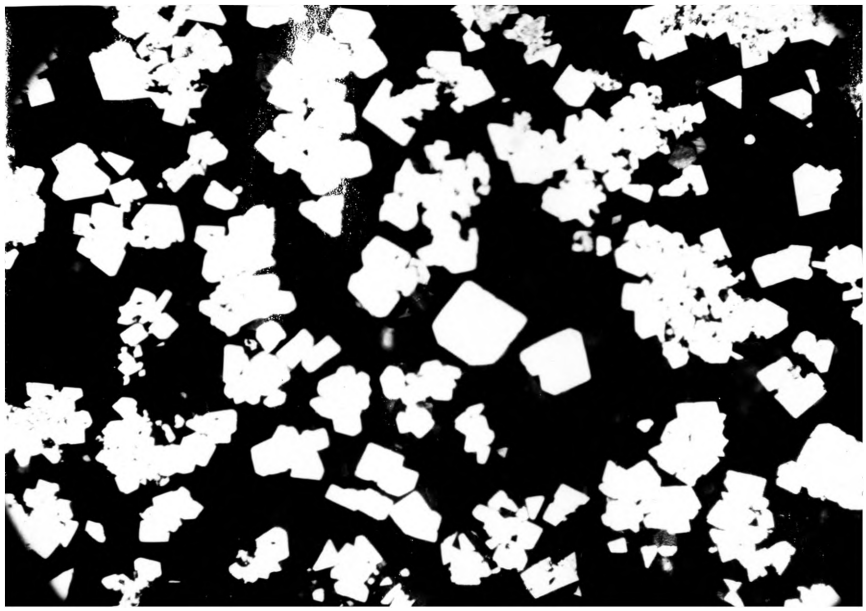


Figure 6-a

Synthetic pyrite No. A-5, prepared by WÖHLER's method. Reflected light, enlargement 350 x .

Figure 6-b

Synthetic pyrite No. A-6 produced by WÖHLER's method. Cubic and octahedral faces are seen. Reflected light, 750 x .

D. Decomposition of Pyrite

A few experiments on the subject of the decomposition of pyrite were carried out. The results showed that pyrites usually decomposed at 625°C in a vacuum. The data of this study are listed in TABLE VIII.

E. Synthetic Cattierite (CoS_2)

The lattice parameter of synthetic cattierite (CoS_2) was determined to be 5.52508 kX at 25°C and the thermal linear expansion coefficient of it was found to be 13.76 x 10^{-6} deg^{-1}. These data are given in Figure 7 and in the Appendix, also in TABLE IV-e.

The crystalline powder of this synthetic cattierite was examined under the ULTROPAK and a regular microscope. The grains appear to be similar to pyrite crystals. As shown in the micro-photos and the direct one to one photographs, the grain size of the cattierite was much smaller (see Figure 8).

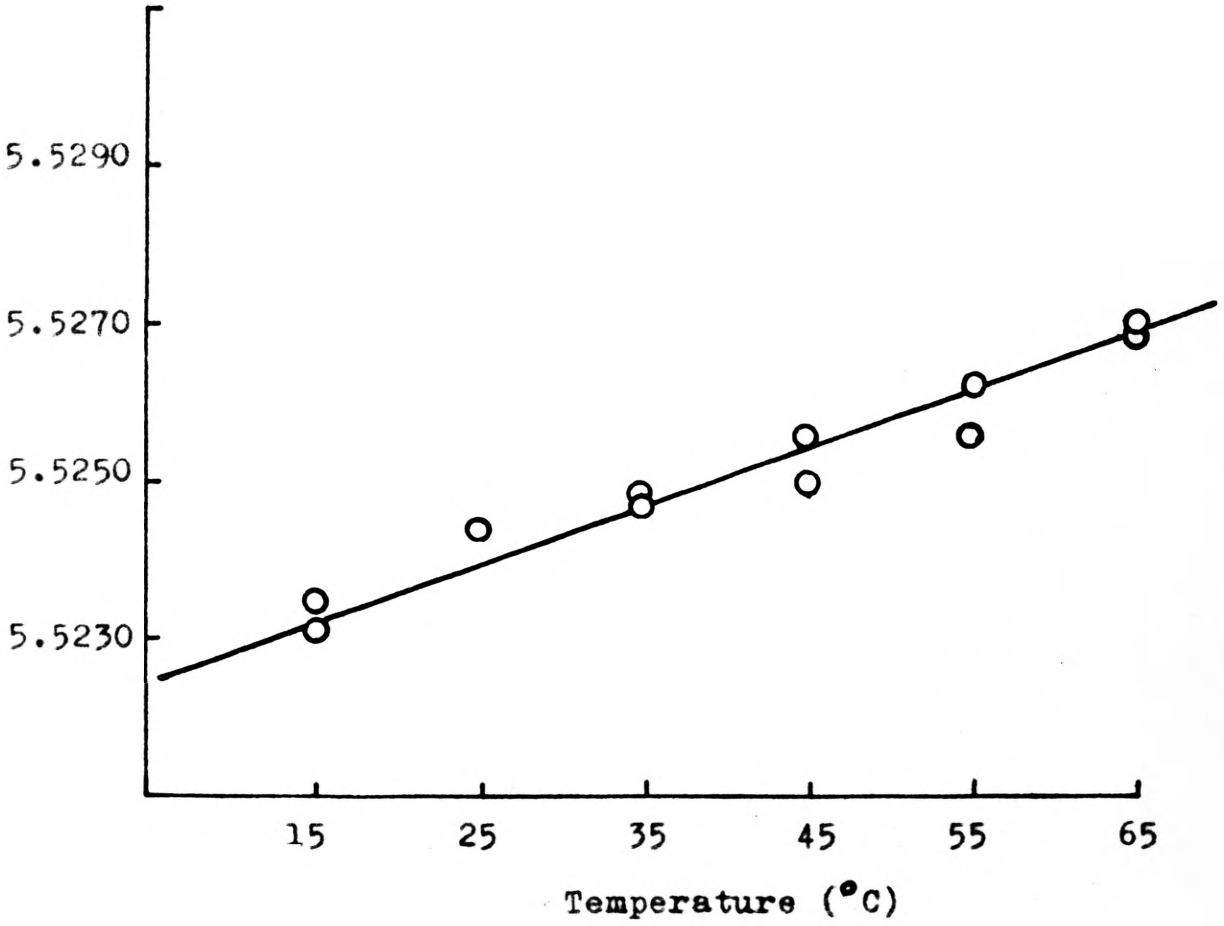
F. Solid Solutions of FeS_2-CoS_2

A series of solid solutions of FeS_2-CoS_2 were prepared in a composition intervals of 10 per cent by weight. The complete series so obtained shows a straight line (as shown in Figure 9).

As the intermediate solid solution $(Fe,Co)S_2$ is far away from the two end members FeS_2 and CoS_2, the diffusion during heating is probably incomplete; the solid solutions formed are distorted and the X-ray pictures become blurred. Figure 10 shows the respective X-ray patterns.

Figure 7

Lattice Parameters of CoS_2
at Various Temperatures



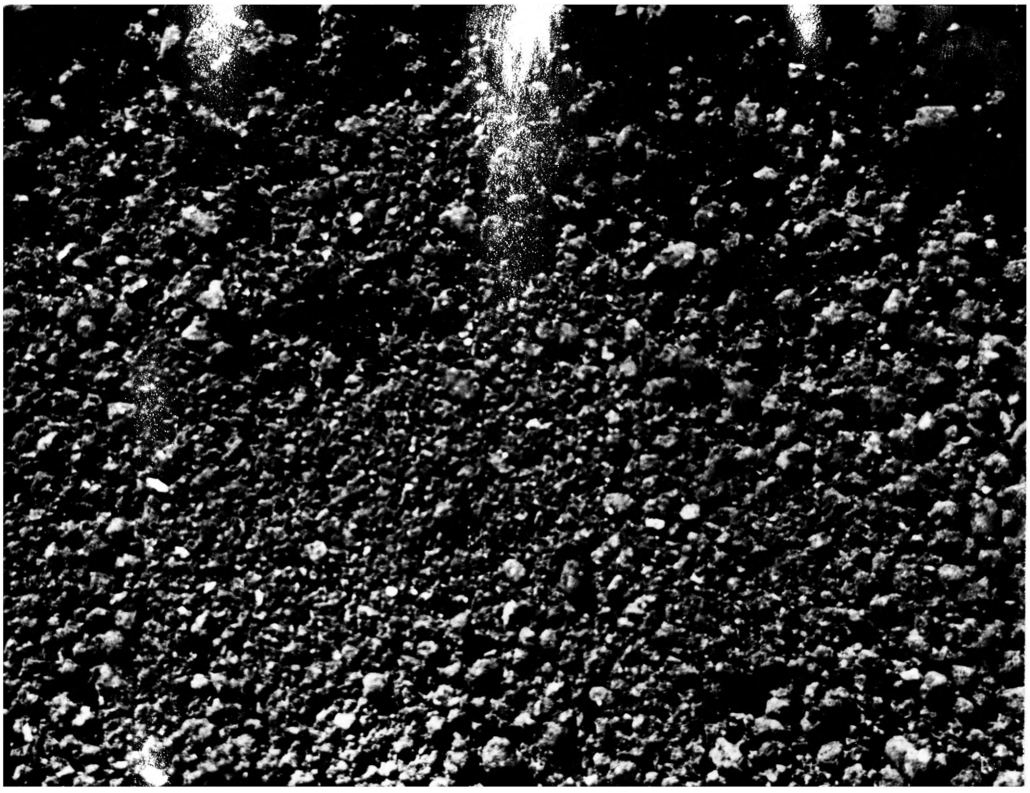


Figure 8-a

Aggregates and individual crystals of the fine grained synthetic cattierite.
Direct one to one photograph, enlargement 4 x linear.

Figure 8-b

Aggregates of synthetic cattierite. Individual grains show indistinct crystal forms. Direct one to one photograph, enlargement 8 x linear.

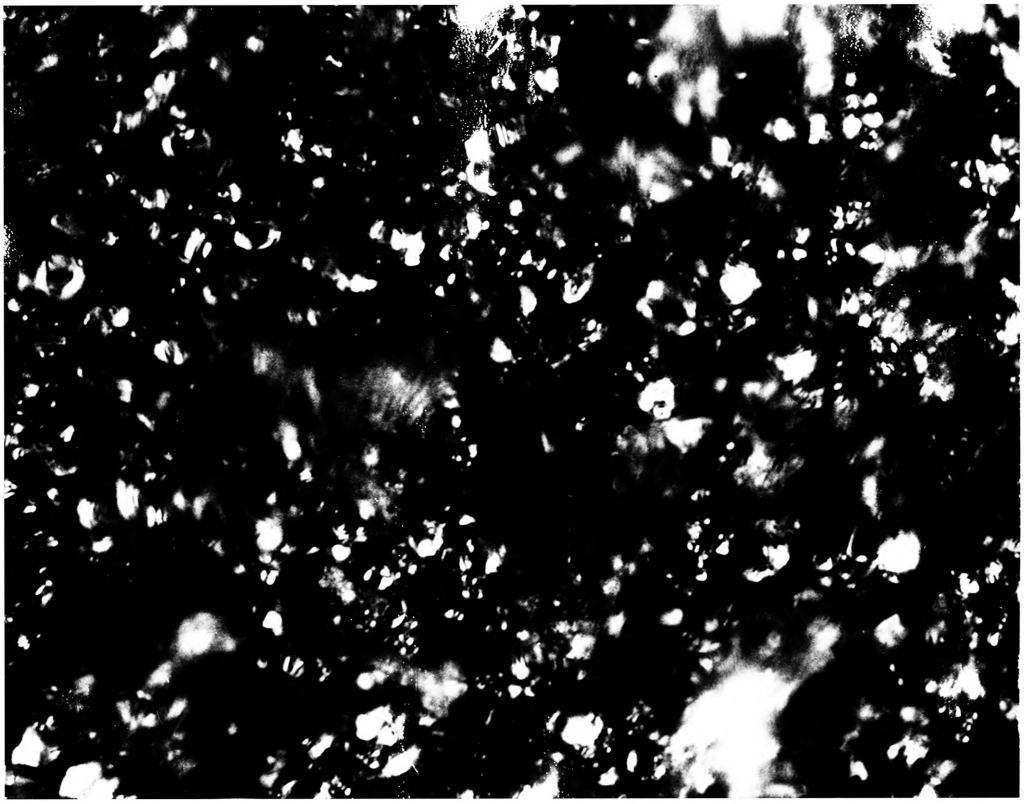
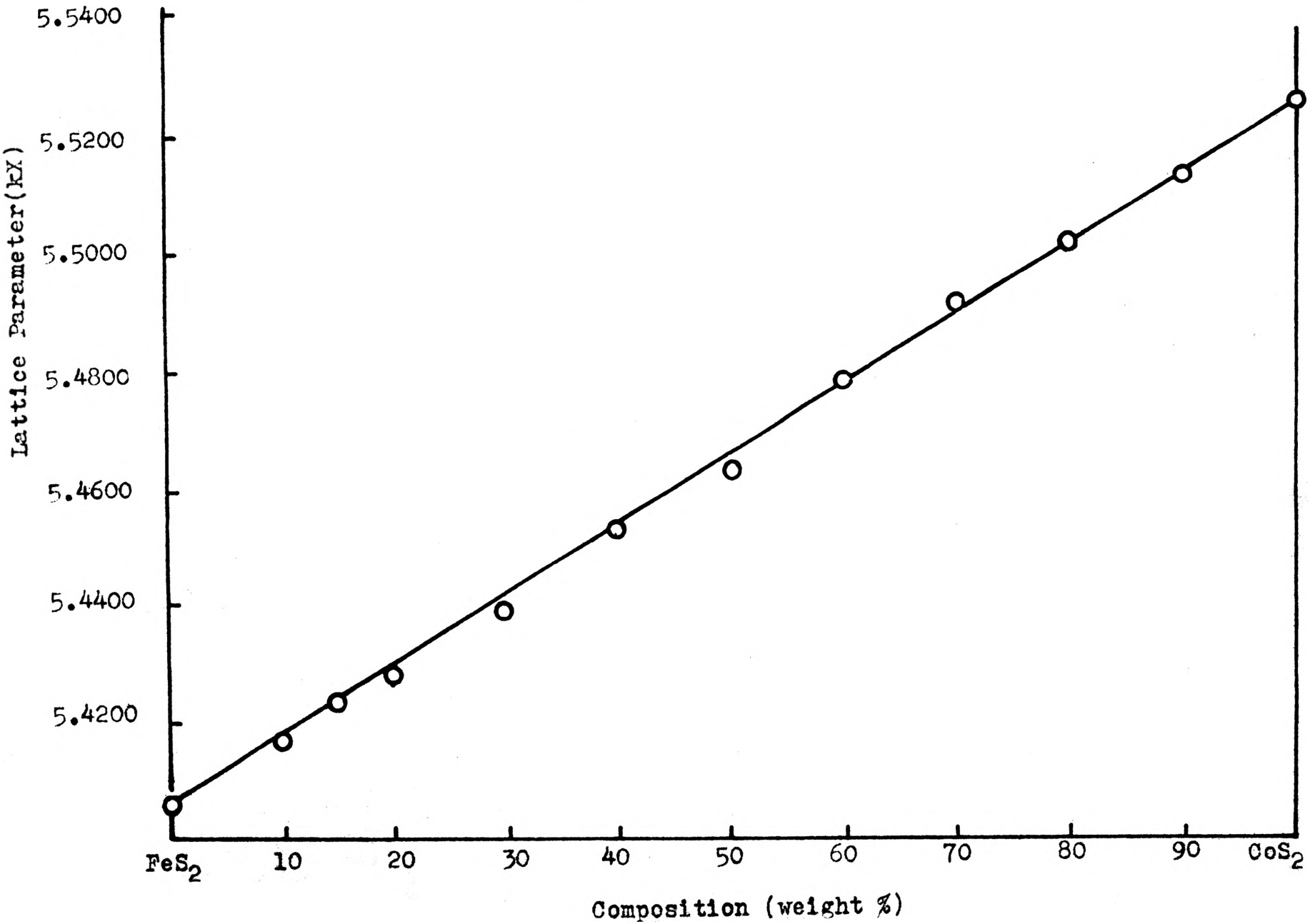


Figure 8-c

Cubes of synthetic cattierite, showing some striations. Note the blurred spots caused by the internal reflections in the splinters of Pyrex glass. ULTROPAK, reflected light, 300 x .

Figure 9

Solid Solubility of FeS_2-CoS_2



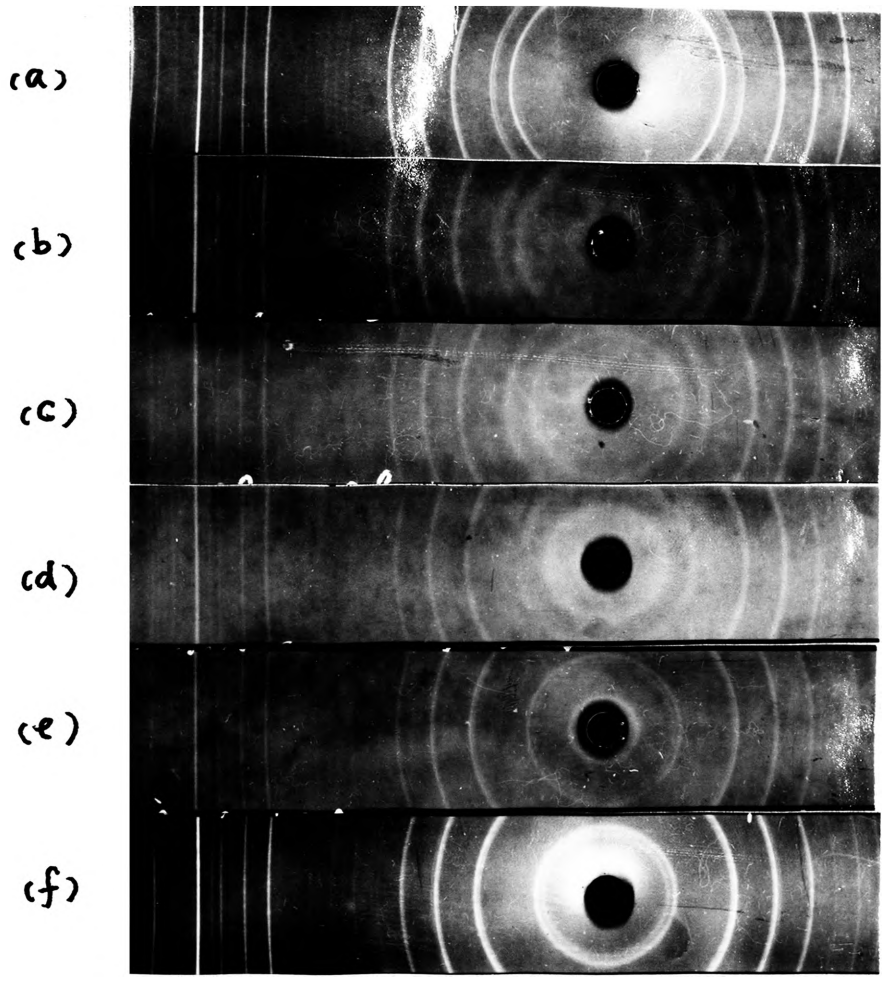


Figure 10

The comparisons of the back reflection lines of the x-ray pictures of the FeS_2-CoS_2 mixed crystals. (a) 100 Wt.% of CoS_2, (b) 70 Wt.% of CoS_2,(c) 50 Wt.% of CoS_2,(d) 30 Wt. % of CoS_2,(e) 10 Wt.% of CoS_2,(f) 100 Wt.% of FeS_2.

CHAPTER V.

DISCUSSION AND COMPARISON OF THE EXPERIMENTAL RESULTS

A. Synthesis

The synthetic work consisted of three major parts; One, the preparation of pure pyrite; two, the preparation of pure CoS_2; and three, the preparation of solid solutions between pyrite and cobalt disulfide.

The procedures of preparing the samples as well as the individual results were somewhat different in each case. In the following, the discussion of these procedures and results is accordingly divided into three parts.

1. Pure synthetic pyrite

(a) In using WÖHLER's method a satisfactory control of vapor pressure of SO_2 during the synthesis of pyrite could not be maintained, even though the composition of the reactants, the temperatures of heating, the initial pressures inside the sealed pyrex tubes, and the dimensions of the tubes were either held constant or accurately measured. This difficulty of control was evidently caused by many other technical factors.

For example, in using WÖHLER's method to prepare pyrite, the pyrex tubes could be inserted only one-third of their length into the furnace in order to prevent an explosion which might have been caused by rapid increases and expansions of the gases in the sealed, insufficient large space. The vapor pressures of SO_2 could by no means

then be kept uniform or constant inside the tube throughout the experiments owing to the existence of such a space with inhomogeneous conditions.

Also, the thick deposition of NH_4Cl on the cooler ends of the inner walls of the sealed pyrex tubes at different places in various experiments could have affected the magnitudes of the vapor pressure of SO_2. This is one difficulty in estimating the vapor pressure.

(b) The technique of using collapsible tubes (KULLERUD & YODER 1959) in order to maintain constant pressures on the samples has not been employed. The investigations here reported were carried out with rigid tubes. The outside pressure was always atmospheric, whereas the inside pressures could not be controlled.

KULLERUD and YODER(1955), reported difficulties when working with low pressures, but, technical details were not disclosed. Also, these investigators worked almost always with high pressures. Therefore, a comparison between the difficulties of the present work and those of the authors can not be made. Differences between the results of the present investigation and those obtained under high pressure and higher temperature conditions may be expected.

(c) In WÖHLER's method the loss of sulfur from the reacting system through sublimation taking place before the actual reaction of the synthesis of pyrite, often caused the failures of obtaining detectable amounts of

pyrite. Also, in these cases some Fe_2O_3 remained in the tube without reacting. To avoid this, samples were not placed into the furnace until the temperature of the furnace reached 360°C which was the temperature at which the synthesis of pyrite took place at a rapid rate.

(d) The grain sizes of the synthetic pyrite could not be controlled in this investigation owing to the above mentioned difficulties and the narrow range of pressure. The various amounts of air inside the sealed pyrex tubes (from vacuum to 5.3 cm Hg) in various experiments had no obvious influence on the grain sizes of the synthetic products.

The grain sizes of the synthetic pyrites were not uniform even in the same experiment. Some of the coarser grains were approximately 0.2 mm in diameter (in sample No. A-3) and some of the finer ones went through the sieve of 325 mesh. The majority of the grains were of the latter size.

(e) The shapes of the synthetic pyrite crystals were not studied in most of the experiments because of the fine sizes of the grains. In the other samples, cubes, pyritohedra, octahedra and their combinations were all observed (as shown in Figure No. 6)

(f) WÖHLER's method and the method of precipitation of sulfides from solution were essential parts of the synthetic work of pyrite in this investigation. The pyrite crystals formed at 360°C, and at 500°C,

respectively, by these methods were the only phases studied thoroughly. Therefore, any conclusion derived from these experimental data can only represent the characteristics of high-temperature-pyrite.

(g) In WÖHLER's method the remaining NH_4Cl and free sulfur could be removed from the final product (synthetic pyrite) by using distilled water and CS_2. The unreacted Fe_2O_3 and often some glass powder dropped into the tube and got mixed with the products while the pyrex tube was broken for taking out the synthetic pyrite. These foreign substances could only be removed by mechanical separation. Therefore, it was impossible to avoid having some traces of impurities mixed with the synthetic pyrites. These could have produced some additional lines in the X-ray diffraction photographs of pyrite. However, only rarely were such lines seen. The lattice parameters of all the synthetic pyrites did not show any evidence of being influenced by these admixtures.

(h) In the second method of producing pyrite, iron sulfide was first obtained from precipitation and was mixed with sulfur to produce FeS_2. During the latter process of the synthesis, the use of an H_2 atmosphere was necessary, because otherwise FeS_2 would not have formed in larger amounts. The explanation for this may be the ability of H_2 to remove the surface oxide layer from the iron sulfide and increase in this way its reactivity with S.

(i) Iron powder has also been used as a reactant for the synthesis of pyrite; but unfortunately without success. The reason for the failure might be sulfide or oxide formation on the Fe grains, preventing the diffusion of S into the core of the grains.

2. Pure synthetic CoS_2

(a) In order to synthezise CoS_2 according to the procedure described in the previous chapter(III A2) it was necessary to obtain first cobalt sulfide with a sulfur content lower than that of CoS_2. This cobalt sulfide was expected to be the main precipitate from the reaction of cobalt chloride and the ammonium hydrosulfide solutions. The number and kind of sulfides in this precipitate was unknown, and so was its sulfur content.

(b) In order to simplify the conditions of synthesis of CoS_2 the same temperature was maintained in all experiments. The tubes were made as short as possible in order that the whole tube could be put into the furnace. In this way, the temperature could be assumed to be uniform throughout the whole tube. Of course, the walls of the quartz glass vessels had to be strong enough to withstand the pressure developed inside the tubes during heating.

(c) In a few experiments, cobalt powder was mixed with sulfur. Mixtures have been heated in a vacuum, and in H_2 at various rates. Yet, CoS_2 could not be produced in this way. This fact is contradictory

to the literature, which reports that CoS_2 was obtained by using cobalt powder as a reactant. ROSENQVIST, (1962) mixed, reground, and reheated the cobalt and the sulfur several times using much longer times of heating. This may perhaps be one way for obtaining some CoS_2 by the use of cobalt powder as a primary reactant. The reason for the slugishness of this reaction may be the same as discussed in the case of Fe and S.

3. Solid solutions of FeS_2-CoS_2

(a) The procedure of the preparation of FeS - CoS solid solutions was essentially the same as that of the synthesis of CoS_2. Therefore, the experimental precautions in making FeS_2-CoS_2 solid solutions were similar to those during the synthesis of the CoS_2.

(b) Explosion of the tubes occurred many times. The reason may have been that the silica glass tube may not have been properly sealed. As already mentioned, explosions usually occurred just a few minutes after the samples were placed into the hot furnace (from 600° to 700°C).

(c) The color of the FeS_2-CoS_2 mixed crystals changed from greyish yellowish to silvery grey with the increasing percentage of CoS_2.

B. X-ray Investigations

1. Natural and Synthetic Pyrites

The optical spectrum analysis and the many microscopic observations of natural pyrites used as samples

for the X-ray work (sample No. 3, Peru), shows only minute specs of sphalerite in pyrite of the above mentioned locality, amounting to less than 1/1000 by volume. In the spectrum analysis, only very minute traces of Cu, Zn, Ni, Co, and Si were found. These small traces of foreign materials could not give additional lines in powder patterns, but they could change the lattice parameter of FeS_2 because of their partial dissolution in the pyrite lattice. Depending upon the amount of the dissolved admixtures the observed lattice parameter ranged from 5.40642 ± 0.0001 to 5.40651 ± 0.00008 kX (or 5.41743 ± 0.00008 Å) in the 3 samples used. However, within the limits of error, there is no difference. This fact suggests that the lattice parameter of the 3 pure pyrite samples investigated here is only slightly influenced by the presence of the above mentioned impurities. Also the influence of crystal forms (appearance of pyrite in form of cubes, pyritohedra, octahedra etc.) within the sensitivity of the method, is negligeable.

Generally the X-ray diffraction patterns of the synthetic pyrite samples were not as sharp as those of the natural pyrite, which could be noticed well from the last reflection ring ($332\alpha_1$ and α_2) in the back reflection area, which was weak and somewhat blurred (α_1 could not be well distinguished from α_2). In some cases, the last lines could just barely be measured. The explanation to this fact may be that the synthetic pyrites

were formed in a relatively short time in comparison to the natural pyrites which were formed in the crust of the earth through a long geological period. Under these circumstances, the lattices of the synthetic pyrites may not be as regular as those of the natural pyrites, and may be somewhat distorted and contain vacancies.

Nevertheless, the average lattice parameter of synthetic pyrite (by WÖHLER's method) was determined to be 5.40762 ± 0.00049 kX at 25°C (the error was larger than in the case of natural pyrite). In comparison to the lattice parameters of the above mentioned natural pyrites, the lattice parameter of synthetic pyrite has a higher value. For instance, in this investigation the highest possible lattice parameter of natural pyrite within the limit of error is 5.40651 + 0.00008 = 5.40659 kX whereas the lowest possible lattice parameter of synthetic pyrite within the limit of error is 5.40762 - 0.00049 =5.40713kX. Therefore, there is still a significant difference of 0.00054 kX between the lattice parameter of synthetic pyrite and of natural pyrite in the lowest case.

In comparison with the literature data (see TABLE I) the lattice parameters of natural pyrite measured here (5.41740 to 5.41743) had a higher value. The values of the literature vary from 5.40 Å to 5.4079 Å, except the newer ones of R. B. GORDEN (5.4179 ± 0.0003 Å) and H.E. SWANSON (5.417 Å) which are close to the present results. However, most of the data from the literature

were not obtained under the condition of temperature control and the purities of the samples were not defined. Therefore, deviations have to be expected.

The same, concerning temperature control is true for synthetic pyrites. H. LEPP(1956) obtained a value of 5.4176 ± 0.0003 Å for the lattice parameter of this pyrite. G. KULLERUD & H.S. YODER(1959) obtained 5.419 ± 0.002 Å for their synthetic pyrite which was produced under high temperature-high pressure conditions. Synthetic pyrite obtained in the present investigation by WÖHLER's method yielded a value of 5.41854 ± 0.0005 Å. Within the limit of error, this value may be 5.41854 + 0.0005 = 5.41904Å, or, 5.41854 - 0.0005 = 5.41804 Å. Therefore, the value of lattice parameter of the present work does not differ from the lattice parameters obtained by LEPP, KULLERUD and YODER. This indicates that the lattice parameters of synthetic pyrites produced under various pressure conditions and temperatures are the same.

The fact remains, which is in agreement with the measurements of other authors that the lattice parameter of synthetic pyrite (5.41854 ± 0.0005 Å) is larger than the parameter of the less pure natural pyrite(5.41739 Å). This is not easy to explain because if Co or Ni go into pyrite as admixture in solid solution, it increases the parameter, although the ionic radius of Co and Ni is smaller than that of Fe in a divalent state(Fe^{2+} 0.83, Co^{2+} 0.82, Ni^{2+} 0.78). According to PAULING, iron in pyrite is divalent. So, it must be assumed that ~~other~~

impurities other than Co and Ni cause the slight contraction of the lattice of pyrite.

There is no data concerning the thermal expansion coefficient of pyrite in the literature. The coefficients of natural pyrites of the two major crystal forms, cube and pyritohedron, as determined from the expansion of the lattice were similar. They ranged from 8.32×10^{-6} to 9.25×10^{-6} deg.$^{-1}$. The linear thermal expansion coefficient of synthetic pyrites obtained did not differ very much from that of the natural pyrites. The average coefficient of natural pyrites was 8.75×10^{-6} deg^{-1} whereas synthetic pyrite varied from 7.25×10^{-6} to 8.74×10^{-6} (average 8.02×10^{-6}). This difference is, however, insignificant. It may be a matter of experimental error.

The sulfur content of pyrite could be decreased by mechanical grinding. Experimental results of the present work showed that the atomic ratio of iron to sulfur of a rigid piece of pyrite and that one of a fine powder from the same piece was 1:1.994 and 1:1.945, respectively. The ratio in all cases was smaller than 1:2. Thus, there was a deficient S in the natural pyrites investigated.

Natural pyrites have been heated at various temperatures and times inside the evacuated, sealed Pyrex tubes. The experiments indicated that decomposition of pyrite (loss of S, as it depositied on the cooler parts inside the glass tube) started even below 625°C. Above

this value only pyrrhotite remained in the tube, as proved by X-ray patterns. Thus the decomposition of pyrite is complete above 625°C in agreement with previous investigators such as G. KULLERUD and H.S. YODER(1959). Although sulfur started to escape from pyrites in different amoumts in all experiments much below 625°C, the lattice parameter of the pyrite samples did not change indicating that the phase FeS_2 is very narrow. Therefore, it can be asserted that pure pyrite has an exact composition of FeS_2, in agreement with BUERGER (1934), KULLERUD and YODER(1959), but the S deficiency observed is due to the presence of the phase FeS in the pyrite which may be in it in a dispersed form,(pyrrhotite lines broad on the partially decomposed FeS_2 patterns) not observable by the microscope. FeS may be present in the FeS_2 because of easy decomposition:

$$FeS_2 \xrightarrow[a]{} FeS + S$$

as proved by heating in vacuum and by grinding of the pyrite (SO_2 odor).

2. Synthetic cattierite (CoS_2)

(a) The lattice parameter of synthetic cattierite (CoS_2) was determined to be 5.52508 ± 0.00062kX, or 5.53624 Å at 25°C by the writer. In comparison with KLEMM's value (1962),(5.537Å, temperature not mentioned) there is only a difference of 0.0013 Å.

(b) In comparison with the lattice parameter of synthetic pyrite reported here, that of CoS_2 was by

0.11699 Å larger, although the ionic radius of Co^{2+} is smaller than that of Fe^{2+}.

(c) The linear thermal expansion coefficient of synthetic cattierite not mentioned in the literature at all was found to be 13.76×10^{-6} deg $^{-1}$ which was almost twice as large as the linear thermal expansion coefficient of synthetic pyrite (7.26×10^{-6} deg^{-1}) reported in this thesis.

3. Solid Solutions of FeS_2-CoS_2

(a) KLEMM(1962), stated that the solid solution series FeS_2-CoS_2 could only be realized at 700°C, whereas in the present work the components FeS_2 and CoS_2 formed a complete series of solid solutions already at 650°C and the lattice parameter changed along a straight line.

(b) In KLEMM's (1962), experiments the time of heating was 100 hours in all cases, whereas in the writer's experiments time of heating varied from 3 to 70 hours. In general, the longer the duration, the better the mixed crystal may be.

(c) As the binary solution $(Fe,Co)S_2$ is farther away from the end members FeS_2 and CoS_2, the last reflection ring became more blurred so that the lattice parameter of the preparations could only be obtained from calculations based on an approximate reading on the indistinct last reflection. For example FeS_2(30%)-CoS_2(70%) had already a weaker last ring than that of the FeS_2(10%)-CoS_2(90%), as seen in Figure 10.

(d) The writer was able to produce solid solutions of FeS_2-CoS_2 in a relatively short time whereas KLEMM needed a longer time for heating. This may be the advantage of using the method of coprecipitation. The sulfides so produced had finer grains and hence were faster to react.

CHAPTER VI

CONCLUSIONS

Of all the methods used by the writer for the synthesis of pyrite, cattierite, and FeS_2-CoS_2 mixed crystals, the method of precipitation and co-precipitation from solutions is best. The main advantages of this method are: (1) Quantitative analyses of the prepared starting solutions can be easily made; (2) An accurate amount of these solutions for the synthesis can be mixed in any proportion; (3) the distribution of Fe^{2+} and Co^{2+} in the coprecipitates are uniform; (4) chemical reactions take place fast because of the fineness of the grains produced. Therefore, the time of heating can be reduced to a minimum.

The lattice parameter of synthetic pyrite has a higher value than those of the natural pyrites according to the experimental results of the present work. These results are in agreement with the literature. A satisfactory explanation of this fact has not yet been given. The writer can only assume that the contraction of the lattice of the natural pyrite is due to the substitution of Fe ions by tracerelements other than Co^{2+} or Ni^{2+}.

There is no significant change in lattice parameters within the limits of error of synthetic pyrite of various kinds (produced under various temperature-pressure conditions).

There is not much difference in thermal linear expansion coefficients between synthetic and natural pyrite.

Deficiency or loss of sulfur may cause the Fe to S ratio in pyrite to be less than 1:2.0. However, the composition of the purest pyrite may be exactly $FeS_{2.0}$.

The lattice parameter of synthetic cattierite (CoS_2) is by $0.118\,\text{Å}$ higher than that of the synthetic pyrite and the thermal linear expansion coefficient of the latter compound is twice as high as that of the synthetic pyrite produced by the writer. This may suggest that within the FeS_2-CoS_2 system, the higher the value of the lattice parameter is, the larger the expansion coefficient may be. However, this assumption has to be confirmed.

As the intermediate compound $(Fe,Co)S_2$ is farther away from the two end members FeS_2 and CoS_2, the mixed crystals formed are distorted and their X-ray pictures become blurred. It is assumed therefore that the diffusion during heating is probably incomplete, and a longer time of heating is thus needed.

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APPENDIX

Film No. 1713 Composition FeS_2(natural) Temp.10°C

	Front Reflection			Back Reflection		
A	85.389	88.947	92.267	178.751	173.547	165.920
B	29.586	26.055	22.742	136.357	141.525	149.175
C	114.984	114.991	115.009	315.108	315.072	315.095

Difference(in mm) 16.745

Circumference 315.091-114.994=200.097
Factor 0.449782 4θ (in mm) 183.352
θ^o 82.468

a = 5.40549 kX

Film No. 1714 Composition FeS_2(natural) Temp. 10°C

	Front Reflection			Back Reflection		
A	79.560	83.112	86.415	172.866	167.678	160.047
B	23.785	20.245	16.924	130.527	135.673	143.319
C	103.345	103.357	103.339	303.393	303.351	303.366

Difference(in mm) 16.728

Circumference 303.370-103.347=200.023
Factor 0.449948 4θ (in mm) 183.295
θ^o 82.473

a = 5.40542 kX

Film No. 1715 Composition FeS_2(natural) Temp. 10°C

	Front Reflection			Back Reflection		
A	76.413	79.967	83.249	169.593	164.453	156.817
B	20.678	17.143	13.851	127.268	132.455	140.077
C	97.091	97.110	97.100	296.861	296.908	296.894

Difference(in mm) 16.740

Circumference 296.887-97.100=199.787
Factor 4θ (in mm) 183.047
θ 82.458

a = 5.40561 kX

Film No. 1710 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	79.108	82.664	85.990	172.392	167.224	159.633
B	23.282	19.768	16.460	130.004	135.152	142.745
C	102.390	102.432	102.450	302.396	302.376	302.378

Difference(in mm) 16.888

Circumference 302.383-102.423=199.960
Factor 0.450090 4θ (in mm) 183.072
θ° 82.398

a = 5.40636 kX

Film No. 1711 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	76.927	80.452	83.779	170.152	165.002	157.419
B	21.200	17.652	14.347	127.804	132.937	140.551
C	98.127	98.104	98.126	297.956	297.939	297.970

Difference(in mm) 16.868

Circumference 297.955-98.119=199.836
Factor 0.450369 4θ (in mm) 182.968
θ° 82.403

a = 5.40630 kX

Film No. 1712 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	77.024	80.593	83.900	170.286	165.100	157.525
B	21.332	17.775	14.483	127.918	133.098	140.680
C	98.356	98.368	98.383	298.204	298.198	298.205

Difference(in mm) 16.845

Circumference 298.202-98.369=199.833
Factor 0.450376 4θ (in mm) 182.988
θ 82.413

a = 5.40618 kX

Film No. 1698 Composition FeS_2(natural) Temp. 35°C

	Front Reflection			Back Reflection		
A	74.559	78.099	81.407	167.881	162.722	155.166
B	18.770	15.245	11.929	125.446	130.590	138.180
C	93.329	93.344	93.336	293.327	293.312	293.346

Difference(in mm) 16.986

Circumference 293.328-93.336=199.992
Factor 0.450018

$4\theta^\circ$ (in mm) 183.006
82.356

a = 5.40689 kX

Film No. 1699 Composition FeS_2(natural) Temp. 35°C

	Front Reflection			Back Reflection		
A	71.737	75.656	79.194	168.923	163.806	156.187
B	23.905	19.982	16.470	125.524	131.665	139.263
C	95.642	95.638	95.664	295.447	295.471	295.450

Difference(in mm) 16.924

Circumference 295.456-95.648=199.808
Factor 0.450432

$4\theta^\circ$ (in mm) 182.884
82.377

a = 5.40663 kX

Film No. 1700 Composition FeS_2(natural) Temp. 35°C

	Front Reflection			Back Reflection		
A	71.780	75.728	79.275	169.027	163.884	156.330
B	23.942	20.025	16.485	126.682	131.816	139.377
C	95.722	95.753	95.760	295.709	295.702	295.707

Difference(in mm) 16.952

Circumference 295.706-95.745=199.961
Factor 0.450088

$4\theta^\circ$ (in mm) 183.008
82.369

a = 5.40673 kX

Film No. 1701 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	75.884	79.430	82.730	169.192	164.031	156.470
B	20.150	16.592	13.320	126.768	131.901	139.450
C	96.034	96.022	96.050	295.960	295.932	295.920

Difference(in mm) 17.020

Circumference 295.937-96.035=199.902
Factor 0.450220 4θ (in mm) 182.882
θ° 82.337

a = 5.40714 kX

Film No. 1702 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	77.135	80.666	83.977	170.380	165.231	157.666
B	21.400	17.854	14.557	127.934	133.077	140.637
C	98.535	98.520	98.534	298.314	298.308	298.303

Difference(in mm) 17.029

Circumference 298.308-98.529=199.778
Factor 0.450500 4θ (in mm) 182.749
θ° 82.328

a = 5.40725 kX

Film No. 1703 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	77.197	80.756	84.074	170.537	165.365	157.832
B	21.555	18.013	14.684	128.086	133.245	140.781
C	98.752	98.769	98.758	298.623	298.610	298.613

Difference(in mm) 17.051

Circumference 298.615-98.759=199.856
Factor 0.450324 4θ (in mm) 182.805
θ° 82.321

a = 5.40734 kX

Film No. 1704 Composition FeS_2(natural) Temp. 55°C

	Front Reflection			Back Reflection		
A	81.234	84.788	88.103	174.513	169.396	161.861
B	25.520	22.000	18.671	132.065	137.157	144.710
C	106.754	106.788	106.774	306.578	306.553	306.571

Difference(in mm) 17.151

Circumference 306.567-106.772=199.795
Factor 0.450462 4θ (in mm) 182.644
θ^o 82.274

a= 5.40794 kX

Film No. 1705 Composition FeS_2(natural) Temp. 55°C

	Front Reflection			Back Reflection		
A	76.855	80.395	83.710	170.054	164.884	157.393
B	21.218	17.700	14.358	127.618	132.654	140.271
C	98.073	98.095	98.068	297.672	297.654	297.664

Difference(in mm) 17.122

Circumference 297.663-98.079=199.584
Factor 0.450938 4θ (in mm) 182.462
θ^o 82.279

a = 5.40787 kX

Film No. 1706 Composition FeS_2(natural) Temp. 55°C

	Front Reflection			Back Reflection		
A	75.951	79.470	82.773	169.172	164.057	156.538
B	20.257	16.752	13.455	295.902	295.908	295.908
C	96.208	96.222	96.228	295.902	295.908	295.908

Difference(in mm) 17.168

Circumference 295.906-96.219=199.687
Factor 0.450705 4θ (in mm) 182.519
θ^o 82.262

a = 5.40809 kX

Film No. 1707 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	69.859	73.766	77.299	167.041	161.925	154.438
B	21.991	18.072	14.553	124.593	129.711	137.211
C	91.850	91.838	91.852	291.634	291.636	291.649

Difference(in mm) 17.227

Circumference 291.639-91.847=199.792
Factor 0.450468

$4\theta^\circ$ (in mm) 182.565
82.239

a = 5.40839 kX

Film No. 1708 Composition FeS_2(natural) Temp.65°C

	Front Reflection			Back Reflection		
A	71.409	75.307	78.838	168.437	163.315	155.791
B	23.575	19.621	16.117	126.008	131.122	138.627
C	94.984	94.928	94.955	294.445	294.437	294.418

Difference(in mm) 17.164

Circumference 294.433-94.955=199.478
Factor 0.451177

$4\theta^\circ$ (in mm) 182.314
82.256

a = 5.40817 kX

Film No. 1709 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	79.094	82.651	85.944	172.421	167.266	159.757
B	23.393	19.830	16.561	129.921	135.052	142.555
C	102.487	102.481	102.505	302.342	302.318	302.312

Difference(in mm) 17.202

Circumference 302.324-102.491=199.833
Factor 0.450376

$4\theta^\circ$ (in mm) 182.631
82.253

a = 5.40821 kX

Film No. 1746 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	83.316	86.842	90.163	176.424	171.290	163.680
B	27.715	24.205	20.890	134.140	139.275	146.884
C	111.031	111.047	111.053	310.564	310.565	310.564

Difference(in mm) 16.796

Circumference 310.564-111.044=199.520
Factor 0.451083 4θ(in mm) 182.724
θ^o 82.424

a = 5.40604 kX

Film No. 1747 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	78.914	82.471	85.763	172.074	166.928	159.380
B	23.390	19.843	16.542	129.792	134.936	142.485
C	102.304	102.314	102.305	301.866	301.864	301.865

Difference(in mm) 16,895

Circumference 301.865-102.307=199.558
Factor 0.450997 4θ(in mm) 182.663
θ^o 82.380

a= 5.40659 kX

Film No. 1744 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	82.416	85.948	89.270	175.620	170.478	162.910
B	26.790	23.260	19.938	133.210	138.344	145.915
C	109.206	109.208	109.208	308.830	308.822	308.825

Difference(in mm) 16.995

Circumference 308.826-109.207=199.619
Factor 0.450859 4θ(in mm) 182.624
θ^o 82.337

a = 5.40714 kX

Film No. 1745 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	79.182	82.706	86.020	172.565	167.421	159.815
B	23.520	20.016	16.692	130.100	135.235	142.840
C	102.702	102.722	102.712	302.665	302.656	302.655

Difference(in mm) 16.975

Circumference 302.658-102.712=199.946
Factor 0.450122

4θ(in mm) 182.971
θ° 82.359

a = 5.40686 kX

Film No. 1742 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	69.792	73.705	77.210	167.025	161.900	154.420
B	21.930	18.018	14.516	124.532	129.648	137.200
C	91.722	91.723	91.726	291.557	291.548	291.620

Difference(in mm) 17.220

Circumference 291.575-91.723=199.852
Factor 0.450333

4θ(in mm) 182.632
θ° 82.245

a = 5.40831 kX

Film No. 1743 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	71.308	75.242	78.776	168.710	163.556	156.025
B	23.554	19.622	16.080	126.152	131.301	138.830
C	94.862	94.864	94.856	294.862	294.857	294.855

Difference(in mm) 17.195

Circumference 294.858-94.861=199.997
Factor 0.450007

4θ(in mm) 182.802
θ° 82.262

a = 5.40809 kX

Film No. 1758 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	78.166	81.702	85.020	171.550	166.405	158.765
B	22.610	19.063	15.765	129.123	134.287	141.900
C	100.776	100.765	100.785	300.673	300.692	300.665

Difference(in mm) 16.865

Circumference 300.676-100.775=199.901
Factor 0.450223

4θ(in mm) 183.036
θ° 82.407

a = 5.40626 kX

Film No. 1759 Composition FeS_2(natural) Temp. 25°C

	Front Reflection			Back Reflection		
A	72.335	76.260	79.800	169.505	164.345	156.755
B	24.860	20.600	17.065	127.148	132.298	139.902
C	96.860	96.860	96.865	296.653	296.643	296.657

Difference(in mm) 16.853

Circumference 296.651-96.862=199.789
Factor 0.450475

4θ(in mm) 182.936
θ° 82.408

a = 5.40624 kX

Film No. 1760 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	71.214	75.135	78.664	168.495	163.340	155.815
B	23.450	19.532	16.000	126.060	131.205	138.760
C	94.664	94.667	94.664	294.555	294.545	294.575

Difference(in mm) 17.055

Circumference 294.558-94.665=199.893
Factor 0.450241

4θ(in mm) 182.838
θ° 82.321

a = 5.40734 kX

Film No. 1761 Composition FeS_2(natural) Temp. 45°C

	Front Reflection			Back Reflection		
A	81.152	84.707	88.008	174.540	169.395	161.840
B	25.498	21.945	18.654	132.065	137.224	144.775
C	106.650	106.652	106.662	306.605	306.619	306.615

Difference(in mm) 17.065

Circumference 306.613-106.654=199.959
Factor 0.450092

$\frac{4\theta}{\theta^\circ}$(in mm) 182.894
82.319

a = 5.40737 kX

Film No. 1762 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	79.154	82.704	86.026	172.505	167.370	159.820
B	23.628	20.078	16.755	129.992	135.149	142.666
C	102.782	102.782	102.781	302.497	302.519	302.486

Difference(in mm) 17.154

Circumference 302.501-102.782=199.719
Factor 0.450633

$\frac{4\theta}{\theta^\circ}$(in mm) 182.565
82.270

a = 5.40799 kX

Film No. 1763 Composition FeS_2(natural) Temp. 65°C

	Front Reflection			Back Reflection		
A	71.480	75.410	78.935	168.820	163.735	156.190
B	23.756	19.810	16.300	126.350	131.463	138.995
C	95.236	95.220	95.235	295.170	295.198	295.185

Difference(in mm) 17.195

Circumference 295.184-95.230=199.954
Factor 0.450104

$\frac{4\theta}{\theta^\circ}$(in mm) 182.759
82.261

a = 5.40811 kX

Film No. 1690 Composition FeS_2(Synthetic) Temp.10°C

	Front Reflection			Back Reflection		
A	74.741	78.304	81.620	168.161	163.068	155.418
B	19.137	15.585	12.276	125.719	130.845	138.384
C	93.878	93.889	93.896	293.880	293.913	293.802

Difference(in mm) 17.034

Circumference 293.865-93,887=199.978
Factor 0.450049 4θ (in mm) 182.944
θ° 82.334

a = 5.40717 kX

Film No. 1691 Composition FeS_2(Synthetic) Temp.10°C

	Front Reflection			Back Reflection		
A	68.763	72.657	76.210	166.056	160.892	153.393
B	20.896	16.958	13.400	123.652	128.828	136.389
C	89.659	89.615	89.610	289.708	289.720	289.782

Difference(in mm) 17.004

Circumference 289.736-89.628=200.108
Factor 0.449757 4θ (in mm) 183.104
θ° 82.352

a = 5.40695 kX

Film No. 1692 Composition FeS_2(Synthetic) Temp.10°C

	Front Reflection			Back Reflection		
A	68.551	72.445	75.984	165.854	160.748	153.177
B	20.737	16.790	13.238	123.468	128.610	136.185
C	89.288	89.235	89.222	289.322	289.358	289.362

Difference(in mm) 16.992

Circumference 289.347-89.248=200.099
Factor 0.449777 4θ(in mm) 183.107
θ° 82.357

a = 5.40688 kX

Film No. 1687 Composition FeS_2(Synthetic) Temp. 25°C

	Front Reflection			Back Reflection		
A	76.377	79.945	83.290	169.702	164.561	157.060
B	20.856	17.323	14.016	127.311	132.443	139.948
C	97.233	97.268	97.306	297.013	297.004	297.008

Difference(in mm) 17.112

Circumference 297.008-97.269=199.739
Factor 0.450588

4θ(in mm) 182.627
θ^0 82.289

a = 5.40775 kX

Film No. 1689 Composition FeS_2(Synthetic) Temp. 25°C

	Front Reflection			Back Reflection		
A	69.194	73.108	76.652	166.487	161.380	153.848
B	21.394	17.454	13.904	124.064	129.215	136.748
C	90.588	90.562	90.556	290.551	290.595	290.596

Difference(in mm) 17.100

Circumference 290.580-90.568=200.012
Factor 0.449973

4θ(in mm) 182.912
θ^0 82.305

a = 5.40755 kX

Film No. 1673 Composition FeS_2(Synthetic) Temp. 35°C

	Front Reflection			Back Reflection		
A	72.010	75.914	79.447	169.305	164.080	156.654
B	24.157	20.231	16.680	126.841	132.074	139.502
C	96.167	96.145	96.127	296.146	296.154	296.156

Difference(in mm) 17.152

Circumference 296.152-96.146=200.006
Factor 0.449987

4θ(in mm) 182.854
θ^0 82.282

a = 5.40783 kX

Film No. 1675 Composition FeS_2(Synthetic) Temp. 35°C

	Front Reflection				Back Reflection			
A	70.030	71.284	73.933	77.485	171.465	167.211	162.084	154.650
B	22.223	20.991	18.289	14.725	120.632	124.825	130.006	137.450
C	92.253	92.275	92.222	92.210	292.097	292.036	292.090	292.100

Difference(in mm) 17.200

Circumference 292.807-92.240=200.567
Factor 0.448727 4θ(in mm) 183.367
θ° 82.282

a = 5.40783 kX

Film No. 1678 Composition FeS_2(Synthetic) Temp. 45°C

	Front Reflection			Back Reflection		
A	76.921	80.483	83.821	170.300	165.214	157.655
B	21.290	17.766	14.464	127.818	132.916	140.475
C	98.211	98.249	98.285	298.118	298.130	298.130

Difference(in mm) 17.180

Circumference 298.126-98.248=199.878
Factor 0.450275 4θ(in mm) 182.698
θ° 82.264

a = 5.40807 kX

Film No. 1679 Composition FeS_2(Synthetic) Temp. 45°C

	Front Reflection			Back Reflection		
A	75.247	78.768	82.085	168.680	163.545	156.024
B	19.600	16.072	12.780	126.199	131.338	138.850
C	94.847	94.840	94.865	294.879	294.883	294.874

Difference(in mm) 17.174

Circumference 294.878-94.850=200.028
Factor 0.449937 4θ(in mm) 182.854
θ° 82.272

a=5.40797 kX

Film No. 1682 Composition FeS_2(Synthetic) Temp. 55°C

	Front Reflection			Back Reflection		
A	76.764	80.314	83.622	170.126	164.948	157.491
B	21.202	17.676	14.355	127.670	132.848	140.290
C	97.966	97.990	97.977	297.796	297.796	297.781

Difference(in mm) 17.201

Circumference Factor: 297.791-97.977=199.814; 0.450419

4θ(in mm) 182.613

θ° 82.252

a=5.40823 kX

Film No. 1683 Composition FeS_2(Synthetic) Temp. 55°C

	Front Reflection			Back Reflection		
A	77.291	80.854	84.135	170.720	165.594	158.086
B	21.704	18.128	14.844	128.152	133.284	140.788
C	98.995	98.982	98.979	298.872	298.878	298.874

Difference(in mm) 17.298

Circumference Factor: 298.874-98.985=199.889; 0.450250

4θ(in mm) 182.591

θ° 82.212

a=5.40874 kX

Film No. 1681 Composition FeS_2(Synthetic) Temp. 55°C

	Front Reflection			Back Reflection		
A	75.653	78.197	81.516	167.998	162.860	155.380
B	18.027	15.500	12.175	125.520	130.657	138.160
C	93.680	93.697	93.691	293.518	293.507	293.540

Difference(in mm) 17.220

Circumference Factor: 293.521-93.689=199.832; 0.450378

4θ(in mm) 182.612

θ° 82.244

a=5.40833 kX

Film No. 1684 Composition FeS_2(Synthetic) Temp. 65°C

	Front Reflection			Back Reflection		
A	70.059	73.966	77.506	171.631	167.424	154.820
B	22.410	18.436	14.882	120.632	124.846	137.475
C	92.469	92.402	92.388	292.263	292.270	292.295

Difference(in mm) 17.345

Circumference Factor: 292.276-92.419=199.857; 0.450322

4θ(in mm) 182.512

θ^0 82.189

a=5.40904 kX

Film No. 1685 Composition FeS_2(Synthetic) Temp. 65°C

	Front Reflection			Back Reflection		
A	76.637	80.204	83.495	174.100	169.865	157.322
B	21.081	17.539	14.247	123.135	127.393	139.963
C	97.718	97.743	97.742	297.235	297.258	297.285

Difference(in mm) 17.359

Circumference Factor: 297.259-97.734=199.525; 0.451071

4θ(in mm) 182.166

θ^0 82.170

a=5.40928 kX

Film No. 1716 Composition FeS_2(Synthetic) Temp. 10°C

	Front Reflection			Back Reflection		
A	78.950	82.510	85.836	172.373	167.265	159.665
B	23.313	19.790	16.472	129.940	135.062	142.646
C	102.263	102.300	102.308	302.313	302.327	302.311

Difference(in mm) 17.019

Circumference Factor: 302.317-102.290=200.027; 0.449939

4θ(in mm) 183.008

θ^0 82.342

a=5.40708 kX

Film No. 1717 Composition FeS_2(Synthetic) Temp. 10°C

	Front Reflection			Back Reflection		
A	78.475	82.006	85.315	171.880	166.746	159.182
B	22.768	19.242	15.935	129.422	134.568	142.130
C	101.243	101.248	101.250	301.302	301.314	301.312

Difference(in mm) 17.052

Circumference 301.309-101.247=200.062
Factor 0.449861

4θ(in mm) 183.010
θ° 82.329

a=5.40724 kX

Film No. 1721 Composition FeS_2(Synthetic) Temp. 25°C

	Front Reflection			Back Reflection		
A	77.150	80.674	83.975	170.304	165.170	157.690
B	21.568	18.040	14.720	298.216	298.197	140.545
C	98.718	98.714	98.695	298.216	298.197	298.235

Difference(in mm) 17.145

Circumference 298.216-98.709=199.507
Factor 0.451112

4θ(in mm) 182.362
θ° 82.266

a=5.40804 kX

Film No. 1722 Composition FeS_2(Synthetic) Temp. 25°C

	Front Reflection			Back Reflection		
A	76.617	80.130	83.443	169.832	164.695	157.160
B	21.056	17.551	14.248	127.365	132.490	140.040
C	97.673	97.681	97.691	297.197	297.185	297.200

Difference(in mm) 17.120

Circumference 297.194-97.681=199.513
Factor 0.451098

4θ(in mm) 182.393
θ° 82.277

a=5.40790 kX

Film No. 1724 Composition FeS_2(Synthetic) Temp. 35°C

	Front Reflection			Back Reflection		
A	69.220	73.141	76.688	166.400	161.280	153.734
B	21.495	17.595	14.047	123.905	129.004	136.545
C	90.715	90.736	90.735	290.305	290.284	290.279

Difference(in mm) 17.189

Circumference 290.289-90.728=199.561
Factor 0.450990 4θ(in mm) 182.372
θ

a=5.40827

Film No. 1727 Composition FeS_2(Synthetic) Temp. 35°C

	Front Reflection			Back Reflection		
A	79.880	83.414	86.726	173.153	168.033	160.526
B	24.313	20.780	17.464	130.690	135.790	143.296
C	104.193	104.194	104.192	303.843	303.823	303.822

Difference(in mm) 17.230

Circumference 303.829-104.193=199.636
Factor 0.450820 4θ(in mm) 182.406
θ 82.232

a=5.40848 kX

Film No. 1729 Composition FeS_2(Synthetic) Temp. 45°C

	Front Reflection			Back Reflection		
A	79.052	82.590	85.908	172.450	167.347	159.790
B	23.433	19.888	16.577	129.876	135.004	142.555
C	102.485	102.478	102.485	302.326	302.351	302.345

Difference(in mm) 17.235

Circumference 302.341-102.483=199.858
Factor 0.450320 4θ(in mm) 182.623
θ^0 82.238

a=5.40839 kX

Film No. 1732 Composition FeS_2(Synthetic) Temp. 45°C

	Front Reflection			Back Reflection		
A	80.063	83.560	86.887	173.362	168.250	160.754
B	24.474	20.963	17.648	130.830	135.951	143.463
C	104.537	104.523	104.535	304.192	304.201	304.217

Difference(in mm) 17.291

Circumference Factor: 304.203-104.532=199.671; 0.450741

4θ(in mm) 182.380

θ° 82.206

a=5.40881 kX

Film No. 1733 Composition FeS_2(Synthetic) Temp. 55°C

	Front Reflection			Back Reflection		
A	81.524	85.051	88.355	174.855	169.795	162.290
B	25.922	22.401	19.100	132.325	137.425	144.900
C	107.446	107.452	107.455	307.180	307.220	307.190

Difference(in mm) 17.390

Circumference Factor: 307.197-107.451=199.746; 0.450572

4θ(in mm) 182.356

θ° 82.164

a=5.40936 kX

Film No. 1734 Composition FeS_2(Synthetic) Temp. 55°C

	Front Reflection			Back Reflection		
A	77.275	80.858	84.125	170.635	165.520	158.062
B	21.756	18.223	14.920	128.060	133.170	140.624
C	99.031	99.081	99.045	298.695	298.690	298.686

Difference(in mm) 17.438

Circumference Factor: 298.690-99.052=199.638; 0.450816

4θ(in mm) 182.200

θ° 82.139

a=5.40968 kX

Film No. 1737 Composition FeS_2(Synthetic) Temp. 65°C

	Front Reflection			Back Reflection		
A	80.818	84.330	87.620	174.190	169.046	161.620
B	25.242	21.720	18.440	131.558	136.688	144.100
C	106.060	106.050	106.060	305.748	305.734	305.720

Difference(in mm) 17.520

Circumference Factor: 305.734-106.057=199.677; 0.450728

4θ(in mm) 182.157

θ° 82.103

a=5.41015 kX

Film No. 1738 Composition FeS_2(Synthetic) Temp. 65°C

	Front Reflection			Back Reflection		
A	78.070	81.600	84.920	171.540	166.380	158.980
B	22.470	18.960	15.655	128.940	133.995	141.445
C	100.540	100.560	100.575	300.480	300.375	300.425

Difference(in mm) 17.535

Circumference Factor: 300.426-100.558=199.868; 0.450297

4θ(in mm) 182.333

θ° 82.104

a=5.41014 kX

Film No. 1739 Composition FeS_2(Synthetic) Temp. 65°C

	Front Reflection			Back Reflection		
A	81.000	84.530	87.840	174.350	169.258	161.840
B	25.475	21.900	18.600	131.802	136.898	144.310
C	106.475	106.430	106.440	306.152	306.156	306.150

Difference(in mm) 17.530

Circumference Factor: 306.152-106.448=199.704; 0.450667

4θ(in mm) 182.174

θ° 82.099

a=5.41021 kX

Film No. 2197 Composition CoS_2(100%) Temp. 15°C

	Front Reflection			Back Reflection		
A	75.840	79.365	82.585	177.075	169.240	161.778
B	21.307	17.866	14.647	120.200	128.040	135.516
C	97.247	97.231	97.232	297.275	297.280	297.294

Difference (in mm) 26.262

Circumference 297.283-97.237 = 200.046
Factor 0.449897

$4\theta^\circ$ (in mm) 173.784
78.185

a = 5.42347 kX

Film No. 2199 Composition CoS_2(100%) Temp. 15°C

	Front Reflection			Back Reflection		
A	75.850	79.294	82.540	177.070	169.258	161.781
B	21.374	17.922	14.680	120.214	128.028	135.502
C	97.224	97.216	97.220	297.284	297.286	297.283

Difference (in mm) 26.279

Circumference 297.284-97.220= 200.064
Factor 0.450006

$4\theta^\circ$ (in mm) 173.785
78.204

a = 5.52308 kX

Film No. 2180 Composition CoS_2(100%) Temp. 35°C

	Front Reflection			Back Reflection		
A	78.209	81.656	84.851	179.310	171.525	165.107
B	23.710	20.259	17.068	122.523	130.307	137.727
C	101.919	101.915	101.919	301.833	301.832	301.834

Difference (in mm) 26.380

Circumference 301.833-101.918 = 199.915
Factor 0.450191

$4\theta^\circ$ (in mm) 173.535
78.124

a =5.52469 kX

Film No. 2181 Composition CoS_2(100%) Temp. 35°C

	Front Reflection			Back Reflection		
A	80.890	84.331	87.545	182.057	174.284	166.837
B	26.352	22.920	19.700	125.195	132.975	140.432
C	107.242	107.251	107.245	307.252	307.259	307.269

Difference (in mm) 26.405

Circumference 307.260-107.246 = 200.014
Factor 0.449968 $4\theta^\circ$ (in mm) 173.609
θ° 78.118

a = 5.52481 kX

Film No. 2184 Composition CoS_2(100%) Temp. 45°C

	Front Reflection			Back Reflection		
A	83.139	86.560	89.784	184.295	176.500	169.065
B	28.651	25.242	22.011	127.425	135.228	142.660
C	111.790	111.802	111.795	311.720	311.728	311.725

Difference (in mm) 26.405

Circumference 311.724-111.796 = 199.928
Factor 0.450162 $4\theta^\circ$ (in mm) 173.523
θ° 78.113

a = 5.52492 kX

Film No. 2185 Composition CoS_2(100%) Temp. 45°C

	Front Reflection			Back Reflection		
A	79.767	83.233	86.460	181.039	173.240	165.820
B	25.198	21.730	18.511	124.100	131.897	139.310
C	104.965	104.963	104.971	305.139	305.137	305.130

Difference (in mm) 26.510

Circumference 305.135-104.966 = 200.169
Factor $4\theta^\circ$ (in mm) 173.659
θ° 78.080

a = 5.52559 kX

Film No. 2188 Composition CoS_2 (100%) Temp. 55°C

	Front Reflection			Back Reflection		
A	77.828	81.299	84.525	178.943	171.195	163.765
B	23.488	20.005	16.790	122.136	129.879	137.310
C	101.316	101.304	101.315	301.079	301.074	301.075

Difference (in mm) 26.455

Circumference 301.076-101.316 = 199.760

Factor 0.450540 $\frac{4\theta}{\theta^\circ}$ (in mm) 173.305 / 78.081

a = 5.52557 kX

Film No. 2189 Composition CoS_2 (100%) Temp. 55°C

	Front Reflection			Back Reflection		
A	76.512	79.962	83.178	177.616	169.849	162.435
B	22.042	18.602	15.380	120.724	128.494	135.900
C	98.554	98.564	98.558	298.340	298.334	298.335

Difference (in mm) 26.535

Circumference 298.336-98.558 = 199.778

Factor 0.450500 $\frac{4\theta}{\theta^\circ}$ (in mm) 173.243 / 78.046

a = 5.52628 kX

Film No. 2193 Composition CoS_2 (100%) Temp 65°C

	Front Reflection			Back Reflection		
A	80.217	83.680	86.930	181.615	173.790	166.437
B	25.757	22.298	19.040	124.608	132.435	139.787
C	105.974	105.978	105.970	306.223	306.225	306.224

Difference (in mm) 26.650

Circumference 306.224-105.974 = 200.250

Factor 0.449438 $\frac{4\theta}{\theta^\circ}$ (in mm) 173.600 / 78.022

a = 5.52677 kX

Film No. 2195 Composition CoS_2(100%) Temp. 65°C

	Front Reflection			Back Reflection		
A	68.296	72.130	75.575	173.169	165.386	158.002
B	21.545	17.719	14.290	116.266	124.057	131.428
C	89.841	89.849	89.865	289.435	289.443	289.430

Difference (in mm) 26.574

Circumference 289.436-89.851 = 199.585

Factor 0.450935 $\frac{4\theta}{\theta^\circ}$ (in mm) $\frac{173.011}{26.574}$

a = 5.52688 kX

Film No. 2161 Composition FeS_2(10%)(CoS_2(90%) Temp. 25°C

	Front Reflection			Back Reflection			
A	72.484	76.345	79.778	173.305	169.132	163.945	161.416
B	25.635	21.772	18.344	124.585	128.760	133.940	136.470
C	98.119	98.117	98.122	297.890	297.892	297.885	297.886

Difference(in mm) 24.946

Circumference 297.888-98.119=199.769
Factor 0.450520 4θ(in mm) 174.823
θ^0 78.761

a = 5.51215 kX

Film No. 2163 Composition FeS_2(20%)(CoS_2(80%) Temp. 25°C

	Front Reflection			Back Reflection			
A	78.535	82.036	85.230	175.250	170.956	165.596	162.970
B	23.754	20.260	17.065	127.037	131.333	136.689	139.318
C	102.289	102.296	102.295	302.287	302.289	302.385	302.288

Difference(in mm) 23.652

Circumference 302.287-102.293=199.994
Factor 0.450014 4θ(in mm) 176.342
θ^0 79.356

a = 5.50109 kX

Film No. 2171 (Approximation) FeS_2(30%)CoS_2(70%) Temp. 25°C

Difference(in mm) 22.400

Circumference 199.854
Factor 0.450329 4θ(in mm) 177.454
θ^0 79.913

a = 5.49132 kX

Film No. 2131 Composition FeS_2(95%)(CoS_2(5%) Temp.25°C

	Front Reflection			Back Reflection		
A	79.736	83.290	86.605	173.162	168.038	160.484
B	23.792	20.237	16.925	130.663	135.790	143.345
C	103.528	103.527	103.530	303.825	303.828	303.829

Difference(in mm) 17.139

Circumference 303.827-103.528=200.299

Factor 0.449328 4θ(in mm) 183.160

θ° 82.299

a = 5.40762 kX

Film No. 2132 Compsoition FeS_2(90%)(CoS_2(10%)Temp.25°C

	Front Reflection			Back Reflection			
A	80.871	84.420	87.744	178.886	174.684	169.709	162.518
B	25.205	21.660	18.335	127.442	131.650	136.630	143.815
C	106.076	106.080	106.079	306.328	306.334	306.339	306.333

Difference(in mm) 18.703

Circumference 306.334-106.078=200.256

Factor 0.449425 4θ(in mm) 181.553

θ° 81.594

a = 5.41705 kX

Film No. 2139 Composition FeS_2(85%)(CoS_2(15%)Temp.25°C

	Front Reflection			Back Reflection			
A	76.335	79.864	83.150	174.440	170.284	165.400	158.434
B	20.472	16.938	13.660	122.710	126.875	131.753	138.724
C	96 .807	96.802	96.810	297.150	297.159	297.153	297.158

Difference(in mm) 19.710

Circumference 297.155-96.806=200.349

Factor 0.449216 4θ(in mm) 180.639

θ° 81.146

a = 5.42348 kX

VITA

Samuel Shu Mou Chan, the eldest son of General and Mrs. Chinan Chan, was born on June 11, 1934, at Hainan Island, China.

His college education began at the Taiwan College of Engineering, Tainan, Taiwan, China, in September, 1953. He received a B. S. degree in Mining and Metallurgical Engineering in June, 1957, from the same college, whose name has since been changed to Taiwan Provincial Cheng Kung University.

He came to the United States in 1958 for graduate study. And, he received a M. S. degree in Mining Engineering from the Missouri School of Mines and Metallurgy in June, 1960.

He is a student member of the Chinese Institute of Mining and Metallurgical Engineers; American Institute of Mining, Metallurgical and Petroleum Engineers; Society of Sigma Xi; Geological Society of America; Mineralogical Society of America; Geochemical Society of America; American Crystallographic Association; and the International Association of Sedimentology.

He has been appointed subsequently as Research Assistant in the Department of Mining Engineering, in the Department of Metallurgical Engineering, and as a Research Fellow in the Department of Geology of Missouri School of Mines and Metallurgy.